[CONTRIBUTION FROM RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Second Ionization Constant of Hydrogen Selenide

BY ROBERT H. WOOD[1]

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The hydrolysis constant of H_2Se has been calculated from the following measurements: (a) the titration curve of H_2Se with potassium hydroxide, (b) the change in *p*H on addition of H_2Se to 0.2 *M* KOH at 0.5°, and (c) the solubility of Na_2Se as a function of the concentration of OH^-. The results are (a) $K_H > 10^{-2}$, (b) for 0.5° and an ionic strength of 0.2, $K_H^{0.2} = 1.1 \pm 0.4$, and (c) for 22° and an ionic strength of 4.2, $K_H^{4.2} = 0.25 \pm 0.09$. From an estimate of the activity coefficients of the various ions and the temperature coefficient of K_2, the second ionization constant of H_2Se (for 22° and zero ionic strength $K_2^0 = 10^{-15.0 \pm 0.6}$) has been calculated. Three methods for the analysis of alkaline solutions of H_2Se have been developed. These methods involve (a) weighing the selenium as the metal, (b) precipitating Ag_2Se, and (c) reduction of I_2 to I^- by the $Se^=$.

This investigation was undertaken to clear up the discrepancy in the values for the second ionization constant of hydrogen selenide. H. Hagisawa reported a value ($K_2 = 10^{-11}$) from a titration curve of H_2Se with sodium hydroxide using a glass electrode.[2] Lingane and Niedrach measured the polarographic waves of H_2Se at various values of *p*H and found for hydrogen selenide $K_2 < 10^{-14}$.[3]

Experimental

Preparation of H_2Se.—The H_2Se used in these experiments was prepared by adding water to aluminum selenide. The aluminum selenide was prepared by the method of G. R. Waitkins and R. Shutt[4] using Fisher certified reagent grade selenium. The manufacturer's analysis gave the sulfur content as 0.05%.

The apparatus for preparing the hydrogen selenide consisted of: (1) a reaction vessel in which oxygen-free water could be added to aluminum selenide; (2) a gas washer containing water; and (3) a reaction vessel containing either sodium or potassium hydroxide. To free the system of oxygen the generator and washer were evacuated and filled with nitrogen and then the reaction vessel was flushed with a steady stream of nitrogen. The nitrogen was freed from all traces of oxygen by passing it over copper at about 300°.

Analysis of ($HSe^- + Se^=$).—Three methods for the analysis of solutions of HSe^- and $Se^=$ were developed. In the first method, the solution to be analyzed is allowed to stand in air until all of the selenium has been oxidized to either selenium metal or selenite. The oxidation to selenite is completed with nitric acid and the selenite reduced to selenium according to the method of Treadwell and Hall,[5] except that the selenium was converted to the grey form by heating to 50 to 60° instead of by boiling the solution. Both $SeO_4^=$ and $SeO_3^=$ are reduced to Se by this method. Table I gives the results of several trial analyses in which pure selenium was used as the starting material. The final volume is the volume of the solution from which the selenium is precipitated. The results show that the analysis is accurate to 0.2% if the final volume is kept at about 50 ml. per gram of selenium.

TABLE I

SELENIUM ANALYSIS NO. 1

Wt. of Se taken, g.	Final vol., ml.	% Recovered
0.8745	50	99.9
.8004	50	100.05
.9019	50	100.25
1.1553	200	99.8
0.8178	400	99.1

The second method of analysis consists of adding a measured volume of the selenide solution to a solution of I_3^- (prepared from IO_3^- and I^-) in acetic acid and potassium iodide. The selenium is oxidized to the metal by the I_3^-. The excess I_3^- is titrated with $S_2O_3^=$, with starch as the indicator. The acid is added to reduce the possibility of reaction of the I_3^- with alkaline $Se^=$ to produce $SeO_3^=$ instead of selenium metal. In the third method, of analysis, a known volume of solution is added to excess $AgNO_3$ in an acetic acid solution. The excess Ag^+ is titrated with standard KSCN, with a silver electrode as an end-point indicator. The acetic acid is used to suppress the formation of Ag_2O and its subsequent coprecipitation. Both these methods of analysis were used by McAmis and Felsing for the analysis of H_2Se solutions, except that McAmis and Felsing weighed the Ag_2Se precipitate, instead of titrating the excess Ag^+.[6] Their results agreed to within 0.2% when aqueous H_2Se was being analyzed. Table II gives the results of several experiments in which the second and third analyses were checked against each other.

TABLE II

ANALYSIS OF ($HSe^- + Se^=$) (NaOH CONCN. = 0.6 *m*)

2 *N* acetic acid, ml.	H_2O, ml.	0.02035 *N* 10_3^-, ml.	0.0200 *N* $AgNO_3$, ml.	Selenium mole × 10^3
10	0		15.01	0.1096
5	5		15.01	.1099
5	5		15.01	.1096
10	5	15.01		.1093
5	5	15.01		.1096

A pipet with a stopcock attached to two side arms was used to transfer the selenium solutions. The solution was drawn up past the stopcock into one arm of the pipet. After the tip of the pipet was wiped off, the solution in the lower part of the pipet was drained using the other side arm to let in air. The pipet was rinsed by first drawing up and returning some of the solution into which it had been drained, and then drawing up distilled water and adding this to the reactants. The volume of the pipet was found by calibration with mercury to be 2.158 ml. A similar pipet with a volume of 6.079 ml. was also constructed for use where the concentration of selenium was small.

The Ag^+ titrations at first gave results that were about 1% high. It was found that, after standing for 1 or 2 days, the solution contained more Ag^+. This effect undoubtedly is due to some coprecipitation of Ag_2O. No further Ag^+ was formed after another week of standing. The final results show that the two methods agree to within 0.2%. When the I_2 titration was checked in 1 *M* KOH solution it was found that a sevenfold excess of I_2 gave results that were 7 to 12% high. A solution of H_2Se in 3.7 *M* NaOH, when titrated with I_3^-, gave answers that increased severalfold as the concentration of I_3^- was increased and concentration of acetic acid was decreased. However, the Ag^+ titrations gave reproducible values, which were about 20% lower than the lowest value obtained with an I_2 titration. The variation of the I_2 results is undoubtedly due to the oxidation of $Se^=$ to SeO_3 by the I_2.

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(1) University of Delaware, Newark, Delaware. Abstracted in part from a thesis, presented by Robert H. Wood, University of California, 1957, University of California Radiation Laboratory Unclassified Document, UCRL-3751.

(2) H. Hagisawa, *Bull. Inst. Phys. Chem. Research, Japan*, **38**, No. 1034.

(3) J. J. Lingane and L. W. Niedrach, THIS JOURNAL, **70**, 4118 (1948).

(4) G. R. Waitkins and R. Shutt, "Inorganic Syntheses," edited by W. C. Fernelius, Vol. II, McGraw-Hill Book Co., New York, N. Y., 1946, p. 184.

(5) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," 9th Edition, John Wiley and Sons, Inc., New York, N. Y., 1955, Vol. 2, p. 107.

pH Measurements.—All pH measurements were made with a Beckman Model GS pH meter with a "blue" glass electrode and a calomel, saturated KCl reference electrode with an asbestos fiber junction. The electrodes were standardized in Beckman buffers.

Titration Curve.—Hydrogen selenide was added to 50.0 ml. of water, and this was titrated with 0.141 *N* KOH.

Glass Electrode Measurements.—In this experiment the change in the pH of KOH solutions after addition of H_2Se was measured. The potassium hydroxide solution was standardized with hydrochloric acid that had previously been standardized against both silver nitrate and potassium hydrogen phthalate. To remove the $CO_3^=$ from the solution some $Ba(OH)_2$ was added. All the experiments were carried out at 0.5 ± 0.5°. After the measurements of the hydrolysis constant, the glass electrode was checked by measuring the pH change on adding standard hydrochloric acid to the potassium hydroxide solution.

Solubility of Na_2Se.—Hydrogen selenide was added to various mixtures of 3.72 *m* sodium hydroxide and 4.32 *m* acetic acid until a precipitate of Na_2Se was obtained. The concentration of selenium in solution was determined by the Ag_2Se method. The solution was sucked up through a medium sintered-glass filter and into the pipet. In all cases the solutions were checked at least a week after being titrated to see if any Ag_2O had dissolved. The silver ion formed in this period was never more than 1% of the total. When an estimate of the amount of sodium selenide precipitated was needed, the solution was stirred rapidly and an unfiltered aliquot taken out and analyzed for selenium. The difference between this analysis and the analysis of the filtered solution gives the amount of Na_2Se precipitated per unit volume of solution. The pH measurements were made after withdrawing a sample of the solution and placing it in a beaker which was constantly swept with nitrogen. The sodium hydroxide solution was analyzed for OH^- and $CO_3^=$ by titrating with standard hydrochloric acid to the phenolphthalein and the brom cresol green end-points. The sodium acetate was analyzed by drying aliquots of the solution to constant weight at 140°.

Results

Titration.—The titration curve is given in Fig. 1. Some selenium (formed by oxidation of H_2Se by traces of O_2) was present in the titration mixture. This selenium originally was present as a grey metal. When the pH of the solution was raised above 8, the selenium began to dissolve to form polyselenides according to the reaction

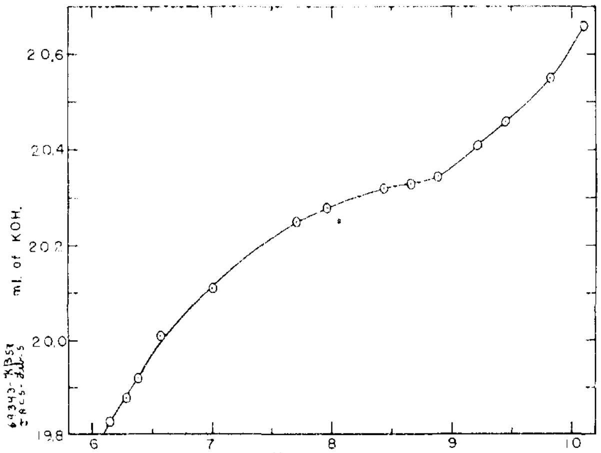

Fig. 1.—Titration of H_2Se with 0.141 *M* KOH.

$$n\mathrm{Se} + \mathrm{HSe}^- \longrightarrow \mathrm{H}^+ + \mathrm{Se}^=_{(n+1)}$$

This reaction is undoubtedly the cause of the discontinuity in the titration curve at pH 8 (see Fig. 1).

The second ionization constant of H_2Se calculated from the first ionization constant ($K_1 = 2.3 \times 10^{-4}$)[6,7] together with the titration curve is $K_2 = 2 \times 10^{-12}$. This value is much too large because of the formation of polyselenide. The formation of polyselenides is quite likely responsible for the value ($K_2 = 10^{-11}$) reported by Hagisawa from a titration curve of H_2Se.[2]

Glass Electrode Measurements.—The data for the addition of H_2Se to 0.2 *m* KOH are given in Table III. In the calibration run the measured pH change is slightly lower than the calculated change. The pH changes measured in the H_2Se experiments have been adjusted for this effect. The adjusted changes in pH are given in the column labeled "Calculated pH." The reasonableness of this assumption is indicated by the observation that in the calibration of the glass electrode at higher concentrations of potassium hydroxide, the measured pH change is increasingly smaller than the calculated pH change. The concentration of selenium was measured by precipitating and weighing the selenium as the metal (see section on analysis for details).

The hydrolysis constant ($K_H^{0.2}$) for the selenide ion at an ionic strength of 0.20 has been calculated using the equations

$$\mathrm{Se}^= + \mathrm{H_2O} \longrightarrow \mathrm{HSe}^- + \mathrm{OH}^-$$

$$K_H^{0.20} = \frac{C_{\mathrm{HSe^-}} C_{\mathrm{OH^-}}}{C_{\mathrm{Se^=}}} = K_H^0 \frac{\gamma^3_{\mathrm{Na_2Se}}}{\gamma^2_{\mathrm{NaHSe}}\gamma^2_{\mathrm{NaOH}}}$$

where K_H^μ is the hydrolysis constant in terms of concentration at an ionic strength of μ and γ is the mean activity coefficient at this concentration. The calculations were made as follows: from the pH change, the change in the concentration of potassium hydroxide was calculated on the assumption that the activity coefficients of H^+ and OH^- remain constant. This assumption is based on the fact that the ionic strength varies very little during the addition of the H_2Se. From the change in concentration of the potassium hydroxide, the moles of H^+ neutralized can be calculated. From this and the total concentration of selenium the concentrations of HSe^- and $Se^=$ were calculated. When attempts were made to use higher concentrations of potassium hydroxide a white precipitate of BaSe was formed (KOH containing no Ba^{++} did not give the precipitate). Because the glass electrode does not work nearly as well in more alkaline solutions, no measurements were made at higher concentrations of OH^-.

Solubility of Na_2Se.—The data on the solubility of Na_2Se as a function of the hydroxide ion concentration are given in Table IV. The calculation of the final concentration of OH^- was made in one of two ways. In experiments 1, 2 and 3, where the concentration of NaOH was fairly high, the concentration of NaOH was calculated by the formula

$$C_{\mathrm{OH^-\,final}} = C_{\mathrm{OH^-\,start}} - C_{(\mathrm{HSe^-} + \mathrm{Se^=})} - \frac{2M_{\mathrm{Na_2Se}}}{V} - C_{\mathrm{Se^=}}$$

where $C_{\mathrm{OH^-}}$ indicates the concentration of the hydroxide ion, etc. The number of moles of sodium selenide precipitated is given by $M_{\mathrm{Na_2Se}}$ and the volume of solution is given by V. The $C_{\mathrm{Se^=}}$ has

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(6) A. J. McAmis and W. A. Felsing, This Journal, **47**, 2635 (1925).

(7) M. d'Hlasko, *J. Chem. Phys.*, **20**, 167 (1923).

TABLE III

GLASS ELECTRODE EXPERIMENTS

Ionic strength = 0.21 ± 0.01

Expt. no.	KOH at start (mole × 10^3)	Δ pH measured	Δ pH calcd.	KOH final (mole × 10^3)	H_2Se added (mole × 10^3)	HSe^- calcd. (mole × 10^3)	$Se^=$ calcd. (mole × 10^3)	Vol. ml.	$K_H^{0.21}$
1	4.26	0.416	0.439 ± 0.01	1.55 ± 0.05	2.52	2.33 ± 0.05	0.19 ± 0.05	20.4	1.0 ± 0.3
2	6.40	.314	.331 ± .1	3.03	3.22	2.97	.25	32.4	1.3 ± 0.5
Calibration	6.52	.296	.313	3.46	..	....	....	..	....
								Weighted av.	1.1 ± 0.4

TABLE IV

SOLUBILITY OF Na_2Se *vs.* C_{OH^-}

Expt. no.	NaOH concn. at start, *m*	Na^+ concn. at start, *m*	Na_2Se concn., *m*	pH	Na^+ concn. final, *m*	(HSe^- + $Se^=$) concn., *m*	$(Na^+)^2$ (HSe^- + $Se^=$) concn., *m*	OH^- concn. final, *m*
1	3.72	3.72	0.02 ± 0.01	....	3.68	0.00524	0.0709	3.67
2	1.40	4.13	.01 ± .005	....	4.11	.00283	.0473	1.37
3	0.370	4.31	.004	....	4.30	.00396	.0732	0.369
4	.130	4.31	.05 ± .01	12.46 ± 0.10	4.21	.01538	.272	.022 ± 0.006
5	.095	4.31	.02 ± .01	11.47 ± .05	4.27	.0590	1.07	.008 ± .002

been calculated by first assuming that it is zero and then calculating the solubility product of Na_2Se. From the solubility product, the concentration of $Se^=$ is calculated and the correction is applied iteratively. In experiments 4 and 5, where the concentration of OH^- is quite low, glass electrode measurements were used for the calculation of the concentration of OH^-. The correction for the effect of Na^+ on the electrodes (0.07 to 0.10 pH) was taken from a graph published by Beckman Instruments, Inc.[8] The activity coefficient of sodium hydroxide in this solution was assumed to be the same as that of sodium hydroxide at the same ionic strength as given by Robinson and Stokes.[9] The activity of the water in this solution was assumed to be the same as in 4.2 *m* NaOH; *i.e.*, 0.85. The results of the calculations are given in Table IV. In experiment no. 1 (in 3.72 *m* NaOH) the analysis was about 1.4 times as high as the value expected on the basis of the other data. This is probably due either to some coprecipitation of Ag_2O with the Ag_2Se or to the formation of $Se_2^=$. This latter explanation is made more probable by the fact that the solution was noticeably yellow, whereas in the other experiments the yellow color, if present, was much lower in intensity. This experiment was discarded in calculating K_{sp} and K_H.

The dependence of the solubility is given by the equations

$$K_{sp} = (C_{Na^+})^2 C_{Se^=}$$

$$K_H = \frac{C_{HSe^-} C_{OH^-}}{C_{Se^=}}$$

or

$$(C_{Se^=} + C_{HSe^-}) = \frac{K_{sp}}{C^2_{Na^+}}\left(1 + \frac{K_H}{C_{OH^-}}\right)$$

or

$$1 = \frac{K_{sp}}{(C_{Na^+})^2(C_{Se^=} + C_{HSe^-})} + \frac{K_{sp}K_H}{(C_{Na^+})^2(C_{Se^=} + C_{HSe^-})(C_{OH^-})}$$

In these equations we assume that if the ionic strength is constant the activity coefficients are also constant. Figure 2 is a plot of

$$1/(C_{Na^+})^2(C_{HSe^-} + C_{Se^=}) \text{ vs. } 1/(C_{Na^+})^2(C_{Se^=} + C_{HSe^-})(C_{OH^-})$$

The intercepts of a straight line drawn through these points should give $(1/K_{sp}K_H)$ and $(1/K_{sp})$, respectively. The two straight lines in Fig. 2 are my estimates of the limits of accuracy with which the points determine a straight line. These lines yield $K_{sp}^{4.2} = 0.040 \pm 0.002$ and $K_H^{4.2} = 0.25 \pm 0.09$. The ionic strength of the solutions is 4.2 ± 0.1.

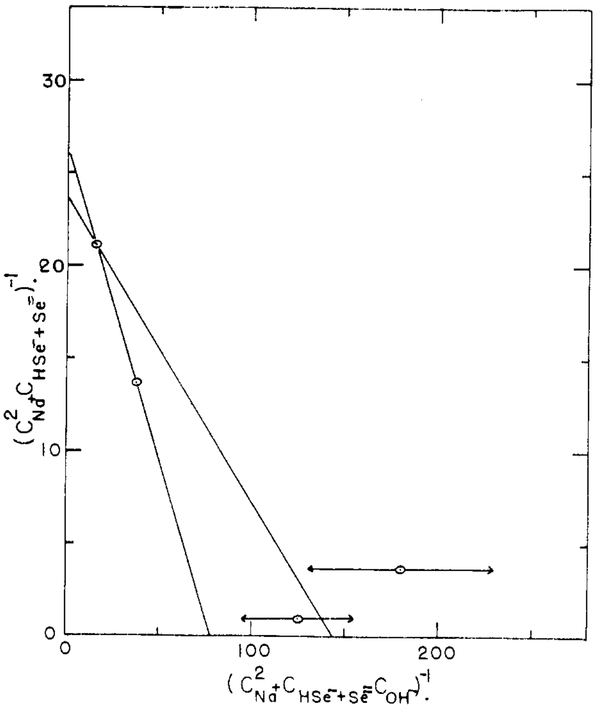

Fig. 2.—Plot of data on Na_2Se solubility as a function of hydroxide concentration.

Interpretation and Discussion

From the two experimental values of the hydrolysis constant ($K_H^{0.2} = 1.1 \pm 0.4$ at 0.5° and

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[8] Beckman Bulletin 100-D, Beckman Instruments, Inc., La Habre, California.

[9] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, New York, N. Y., 1955.

$K_H^{4.2} = 0.25 \pm 0.09$ at 22°) two values of K_H^0 at 22° can be calculated from the usual thermodynamic equations and the assumptions that (a) the activity coefficients of NaHSe and Na_2Se in these solutions are the same as those of NaOH and Na_2SO_4, respectively, at the ionic strength of the solutions, and (b) Latimer's estimates of the entropies of HSe^- and $Se^=$, namely, 22 and 0 e.u., respectively,[10] are correct. These calculations give, from the measurements at 0.5°, $K_2^0 = 10^{-14.5 \pm 0.4}$ at 22°, where the limits of error come from the limits of error of the original measurement and my estimate of the reliability of the above assumptions. The measurement at 22° gives $K_2^0 = 10^{-15.9 \pm 0.8}$. If both measurements are taken into account with their estimated limits of error, the best value is probably $K = 10^{-15.0 \pm 0.6}$.

TABLE V

ACID CONSTANTS OF H_2A

Compound	pK_1	pK_2	$pK_2 - pK_1$	Ref.
H_2O	15.7			
H_2S	7.0	12.9	5.9	11, 12
H_2Se	3.6	15	11.4	6, 7
H_2Te	2.6	11	8.4	7, 3

Table V gives the pKs (where $pK = -\log K$) of several of the acids analogous to H_2Se.

Assuming a simple electrostatic model, one obtains the equations

$$pK_1 = \frac{Cz_1z_2}{r} = \frac{C}{r}$$

$$pK_2 = \frac{Cz_1z_2}{r} = \frac{2C}{r} \text{ and } pK_2 - pK_1 = \frac{C}{r}$$

where C is a constant, z_1 and z_2 are the charges on the ions, and r is the bond length of the atoms. On the basis of this model one would expect that pK_1, pK_2 and $pK_2 - pK_1$ would increase from the heavier members of the series to the lighter members. This does not occur. The discrepancy is shown most distinctly by $pK_2 - pK_1$, where the value is lower for H_2S than for either H_2Te or H_2Se. Therefore, on the basis of this model, one would conclude that the value of K_2 for H_2S is anomalous. The assignment of partially covalent character to the bonds does nothing to help resolve this anomaly.

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BERKELEY, CALIFORNIA

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[11] H. Kubli, *Helv. Chim. Acta*, **29**, 1962 (1946).

[12] N. Konopick and O. Leberl, *Monatsh. Chem.*, **80**, 781 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEMPLE UNIVERSITY]

Phosphine Oxides. V. Intra- and Intermolecular Association[1]

BY CAROLINE D. MILLER,[2,3] ROBERT CLAY MILLER[3] AND WILLIAM ROGERS, JR.

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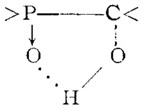
An intramolecular hydrogen bond of the type  has been found in certain α-hydroxy phosphoryl compounds. The strength of this bond has been related to the negativity of the phosphoryl oxygen. When the phosphoryl is extremely polarized, as in the phosphine oxides, an intermolecular association is also observed. This is probably a dipole–dipole interaction of these phosphoryl groups.

The spectra of a number of phosphoryl compounds have appeared recently in the literature, and various assignments have been made, both empirically and theoretically. The effect of electronegativity of the substituents on the phosphoryl stretching frequency has been shown,[4,5] and the existence of hydrogen bonding phenomena involving the phosphoryl group has been demonstrated.[6,7] Analogous relationships involving the carbonyl group have received somewhat more attention; and, with the exception of the steric differences of the tetrahedral phosphorus atom of the phosphoryl from the planar carbon atom of the carbonyl, there exists a notable similarity.

Recent work at this Laboratory has resulted in the synthesis of several new classes of organophosphorus compounds, whose spectra have also been recorded, from which certain information concerning their structure and properties may be deduced. Chronologically the first, and structurally the simplest, of these are the disubstituted phosphine oxides, $R_2P(O)H$. Prior to their general synthesis,[8] such compounds were tentatively classed as trivalent phosphinous acids, $R_2P{-}OH$[9]. However, the presence of strong P–H absorption at 2335 cm.$^{-1}$

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[1] Presented at the Meeting of the American Chemical Society at New York, N. Y., September 1957. For the fourth paper in this series, see R. C. Miller, C. D. Miller, W. Rogers and L. A. Hamilton, THIS JOURNAL, **79**, 424 (1957).

[2] Abstracted in part from the dissertation submitted by C. D. M. to the Temple University Graduate Council in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Experimental Station, E. I. du Pont de Nemours Co., Wilmington, Delaware.

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[7] E. Halpern, J. Bouck, H. Finegold and J. Goldenson, *ibid.*, **77**, 4472 (1955).

[8] R. H. Williams and L. A. Hamilton, *ibid.*, **74**, 5418 (1952).

[9] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950.