

tion mixture. Hence the potential of the latter must be taken as our limit.

The identity of "At(+X)" remains undetermined. HAtO is the most likely species, though HAtO₂ is also a reasonable possibility. It should be borne in mind that "At(+X)" need not represent a single species or even a single oxidation state. Indeed, the nature of the state may vary with the mode of preparation. Under appropriate conditions an interhalogen compound such as AtCl₃ may be present,¹¹ and we can never exclude the possibility of compounds with impurities.

The At(0)-At(+X) potential is about the same whether or not I₂ is present. Both the At₂-At(+X) and the At-At(+X) potentials should be much more positive than the AtI-At(+X) potential, since under our conditions both At₂ and At should be highly unstable with respect to AtI. Hence neither At₂ nor At· can be the predominant At(0) species in the absence of I₂. It seems not at all unlikely that when I₂ is absent, most of the At(0) reacts with impurities to form organic astatine compounds.

The photochemical reactions of astatine with the iron and vanadium couples appear quite remarkable, since they involve a gross shift of a chemical equilibrium under the influence of light. Such an effect is likely only if the reaction under investigation involves a species present at trace concentrations, but the primary photochemical process involves only species present at macro concentrations. Our information on these astatine reactions, however, is insufficient to permit meaningful speculation as to their mechanisms. Nonetheless, these reactions make it clear that serious misinterpretation may result from neglect of photochemical effects on tracer-level studies. Thus Latimer set the At(0)-At(+X) potential at *ca.* -0.7 v.³ on the basis of Johnson, *et al.*'s, report that ferric ion oxidized At(0).⁴ This oxidation is almost certainly the photochemical reaction

(11) H. M. Neumann, *J. Inorg. Nuclear Chem.*, **4**, 349 (1957).

we have examined, and Latimer's potential is therefore not sufficiently negative.

In studying the reduction of At(0), one cannot avoid ambiguity as to the nature of the At(0) species, since any iodine in the system is reduced before the astatine. A discrepancy exists between the results with the As(III)-As(V) couple, which indicate the At-At(0) potential to be about -0.3 v., and the ferrocyanide-ferricyanide results, which suggest -0.4 v. We have favored the former, since there seem yet to be some unanswered questions regarding the ferrocyanide-ferricyanide couple.¹²

In Table I the astatine potentials are compared with those of the other halogens. The astatine values are in general agreement with the trends exhibited by the lighter members of the series, although astatate might seem to be an unduly strong oxidant. This, however, could have been anticipated by analogy with the nitrogen group, in which bismuthate is a much more powerful oxidant than any other +5 state. This discontinuity makes astatine the only halogen with a state between zero and +5 which is stable to disproportionation and is consistent with the tendency among all the main group elements for increasing molecular weight to be accompanied by increasing stabilization of intermediate positive states.

TABLE I

	X ⁻ -X ₂ (aq.)	X ₂ (aq.)-HOX	HOX-HXO ₂	HXO ₂ -HXO ₃
Cl	-1.40	-1.53	-1.35	-1.13
Br	-1.09	-1.51	-1.42
I	-0.62	-1.31	-1.07	(-1.6)
At	(-0.3)	(-1.0)	(-1.5)	<-1.6

Acknowledgments.—I wish to express my gratitude to Professor I. Perlman for his direction of this study and to Professor Robert E. Connick for many helpful discussions.

(12) W. L. Reynolds, *THIS JOURNAL*, **80**, 1830 (1958).

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Acid Hydrolysis of [PtCl₄]⁻ and [PtCl₃(H₂O)]⁻¹

BY CHARLES I. SANDERS AND DON S. MARTIN, JR.

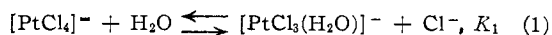
RECEIVED AUGUST 1, 1960

The equilibrium constant for the acid hydrolysis of [PtCl₄]⁻ at 25° is 3.0×10^{-2} at $\mu = 0$ and 1.5×10^{-2} at $\mu = 0.318$. The equilibrium constant for the acid hydrolysis of [PtCl₃(H₂O)]⁻ at 25° is 1.0×10^{-2} at $\mu = 0$ and 5.4×10^{-4} at $\mu = 0.318$. A tentative value of 7.0 is reported for pK'_{11} where K'_{11} is the acid dissociation constant of [PtCl₃(H₂O)]⁻. Tentative values are $pK'_{21} = 5.2$ and $pK'_{22} = 8.3$, where K'_{21} and K'_{22} are the first and second acid dissociation constants for [PtCl₄(H₂O)₂].

Introduction

From earlier isotopic exchange experiments it was reported^{2a} that the acid hydrolysis of [PtCl₄]⁻ was conveniently measurable by a titration with

standard base of the acid formed, which was considered to be the [PtCl₃(H₂O)]⁻ ion. The hydrolysis reaction was written as

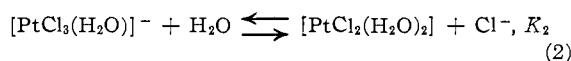


The titration of aged 0.0166 molar solutions of K₂-

(1) (a) Presented at the Symposium on Aqueous Solutions, Division of Inorganic Chemistry, American Chemical Society Meeting at Atlantic City, Sept. 17, 1959. (b) Contribution No. 895. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) (a) L. F. Grantham, T. S. Elleman and D. S. Martin, Jr., *THIS JOURNAL*, **77**, 2965 (1955). (b) W. W. Dunning and D. S. Martin, Jr., *ibid.*, **81**, 3566 (1959).

PtCl₄ at $\mu = 0.318$ indicated K_1 to be 0.018 mole/l. At that time the titrations were not performed for other concentrations. Some exploratory experiments^{2b} in a recent study of the bromide substitution equilibria of [PtCl₄]⁻ and [PtCl₃(H₂O)]⁻ indicated that reaction 1 did not satisfactorily describe the system upon dilution, and the present study was undertaken to determine if an equilibrium constant for a second hydrolysis reaction



might be evaluated.

Experimental

Materials.—The K₂[PtCl₄] was similar to the material used in the earlier work^{2a} except that iridium had been removed by a prior fractional crystallization of K₂[PtBr₆], which has been shown to reduce the Ir content to below 0.05 ppm. Analyses for Pt on separate batches yielded: 45.1 and 46.6%. Calcd., 47.0%.

For ion-exchange experiments an anion exchange resin, Dowex 1, 50–100 mesh, was used. Other reagents were analytical reagent grade which were certified to meet A.C.S. standards. All water was drawn from the distilled water tap and was redistilled from alkaline permanganate solution.

Equipment.—In the acid-base titrations the pH of the solution was determined potentiometrically by means of a Beckman Model "G" pH meter in conjunction with shielded electrodes, Model 1190–80. The instrument was standardized against a Beckman or Fisher pH-7 buffer. The titrations were performed with a Machlett Auto-Burette with divisions for each 0.01 ml. In the gravimetric analyses for platinum, the metal was electroplated onto platinum gauze electrodes by means of a Sargent-Slomin Electrolytic Analyzer.

Procedure.—To prepare a solution, a sample of K₂[PtCl₄] and any salt used to adjust the ionic strength was weighed out and added to a volumetric flask. Water was added to the mark. The flask was placed in a thermostat which controlled temperatures to ± 0.1 , and the solutions were aged to establish the hydrolysis equilibria. Aging time at 25° was 1 to 3 days. In an experiment in which daily samples were taken from a K₂[PtCl₄] solution at 25°, the titers did not change detectably in the period of 1 to 5 days. Over longer periods some decomposition of the compound was apparent from the formation of a solid. Decomposition was somewhat more rapid in solutions with added salt. Of the common anions tested, nitrate gave the slowest decomposition; so the ionic strength was adjusted by the addition of sodium nitrate. After the aging period, 15 ml. samples were withdrawn for the titrations with standard (ca. 0.1N) NaOH. An initial, fairly complete titration requiring ca. 10 min. was performed to locate the end-point. At least two further titrations for each sample were performed in which the end-point was approached rapidly and a number of points in the vicinity of the end-point were obtained quickly. The end-points were taken from plots of the rate of change of pH with respect to added titrant *vs.* the added titrant. Hydrolysis during the period of the titration did not appear to affect seriously the titer of the solutions.

After the titration each solution was acidified with H₂SO₄ and the Pt content was determined by the electrodeposition procedure. In general, the precision of the titrations appeared to be somewhat better than that of the Pt analyses.

Results of the titrations and analyses for individual solutions at 25° have been collected in Table I. The data in Table I are representative and extend over a range of dilutions. In a number of cases additional experiments were performed for concentrations very similar to the ones which have been included. Considerably more data, which are in substantial agreement with those of Table I, are therefore at hand.

Ion Exchange Experiments.—Since [PtCl₂(H₂O)₂] is a neutral species, it should readily penetrate an anion exchanger; whereas [PtCl₄]⁻ and [PtCl₃(H₂O)]⁻ should be strongly retained. The ion exchange experiments were undertaken to confirm the presence of the dichlorodiaquo-platinum(II) species. Two aged solutions, originally 0.001 mole/l. in K₂[PtCl₄], were prepared. One solution had no

TABLE I
ANALYSES AND TITRATION OF AGED SOLUTIONS OF K₂
[PtCl₄] FOR 25°

Total Pt, "a", mole/l. $\times 10^3$	Added KCl "b", mole/l. $\times 10^3$	Ionic strength before aging "μ", mole/l.	Equivalents of acid "T", eq./l. $\times 10^3$	
			Obsd.	Calcd.
No added salt; $K_1 = 3.0 \times 10^{-2}$, $K_2 = 1.0 \times 10^{-3}$				
0.92	0	0.003	1.30	..
4.86	0	.015	4.96	4.90
4.76	2.00	.016	4.51	4.42
9.86	0	.030	8.26	8.27
16.47	0	.049	11.80	..
NaNO ₃ added; $K'_1 = 1.5 \times 10^{-2}$, $K'_2 = 5.4 \times 10^{-4}$				
1.05	0	0.318	1.25	1.28
4.88	0	.318	4.31	..
16.30	0	.318	10.31	..

added salt while the second contained sufficient NaNO₃ to give an ionic strength of 0.318. A 200 ml. sample of the first solution was passed through 20 cm. length \times 1.1 cm. in diam. of Dowex resin in the perchlorate form. The same volume of the NaNO₃-containing solution was passed through a similar column in the nitrate form. Each column was washed with 100 ml. of H₂O which was added to the corresponding eluate. The total Pt eluted from the column in each case was determined. For the solution with no added salt a significant titer for the acid content also was obtained.

Treatment of Data.—The appearance of an acid in the solutions is taken as evidence that an H₂O has replaced Cl⁻ in the coordination complexes and that a proton of the coordinated H₂O has become sufficiently acidic to permit its titration. It can be seen from the data in Table I that the equilibrium ratio of titer:platinum increases with dilution.

If the second acid hydrolysis (eq. 2) does not occur, an equilibrium constant of 0.0178 mole/l. is calculated for eq. 1 by the method of ref. 2a from the titer of 10.31×10^{-3} eq./l. for the 16.30×10^{-3} mole/l. solution of K₂PtCl₄ (Table I). For such a single equilibrium the titer calculated for the 4.88×10^{-3} solution of K₂PtCl₄ is 3.98×10^{-3} eq./l. This calculated titer is nearly 8% less than the observed titer and rather unsatisfactory.

Furthermore, in some cases of high dilutions the ratio of titer:total Pt exceeded 1.0. Since two protons from a single coordinated H₂O cannot generally be titrated with a single break, it has been concluded that ratios of titer:platinum > 1.0 resulted from the formation of significant quantities of [PtCl₂(H₂O)₂] for which a proton from each coordinated H₂O was titrated.

With reference to reactions 1 and 2,

a = conc. K₂[PtCl₄] (mole/l.) in the original solution before aging and therefore the total Pt concn., and

b = conc. KCl (mole/l.) in the original solution. The concentrations can be expressed

$$\begin{aligned} [\text{PtCl}_3(\text{H}_2\text{O})^-] &= x \\ [\text{PtCl}_2(\text{H}_2\text{O})_2] &= y \\ [\text{PtCl}_4^-] &= a - x - y \\ \text{Cl}^- &= b + x + 2y \end{aligned}$$

In accordance with the above assumptions the titer of the acid in the solution, T (eq. acid/l.), was taken as

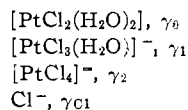
$$T = x + 2y \quad (3)$$

The equilibrium constants for reactions 1 and 2 can be written

$$K_1 = \frac{x(b+x+2y)\gamma_1\gamma_{Cl}}{(a-x-y)\gamma_2} = \frac{x(b+x+2y)}{(a-x-y)\Gamma_1} \quad (4)$$

$$K_2 = \frac{y(b+x+2y)\gamma_0\gamma_{Cl}}{x\gamma_1} = \frac{y(b+x+2y)}{x\Gamma_2} \quad (5)$$

The activity coefficients are for the species



and

$$\begin{aligned} \Gamma_1 &= \gamma_2/\gamma_1\gamma_{Cl} \\ \Gamma_2 &= \gamma_1/\gamma_{Cl}\gamma_0 \end{aligned}$$

From equations 3 and 5 the explicit expressions 6 and 7 for the concentration variables x and y can be written

$$x = T(b+T)/(b+T+2\Gamma_2K_2) \quad (6)$$

$$y = \Gamma_2K_2T/(b+T+2\Gamma_2K_2) \quad (7)$$

Also, the variables x and y can be eliminated between equations 3, 4 and 5 to yield

$$\Gamma_1K_1(b+T)(a-T) + \Gamma_1K_1\Gamma_2K_2(2a-T) = T(b+T)^2 \quad (8)$$

Equation 8 relates the products Γ_1K_1 and Γ_2K_2 to the measurable titer of the solution. The equilibrium constants K_1 and K_2 can be evaluated from the titers of two experiments at different concentrations, provided that Γ_1 and Γ_2 are known for each concentration.

The quantities K'_1 and K'_2 are defined by

$$K'_1 = \Gamma_1K_1 \quad (9)$$

$$K'_2 = \Gamma_2K_2 \quad (10)$$

For solutions at the same ionic strength the quantities K'_1 and K'_2 can be considered constants to the extent that Γ_1 and Γ_2 are functions only of the ionic strength. The experiments in Table I for which NaNO_2 was added were at an ionic strength of 0.318 mole/l. before aging. Since the hydrolysis caused only minor changes in the ionic strength, the quantities K'_1 and K'_2 were taken as constants for these experiments.

For experiments with no electrolyte besides the $K_2[\text{PtCl}_4]$ or KCl the ionic strength, μ , is low but varies strongly with the concentrations and with the hydrolysis according to equation 11.

$$\mu = 3a + b - T + y \quad (11)$$

For these conditions Γ_2 was taken as 1, and for Γ_1 was used the function $f_{\text{C}_2\text{O}_4^-}/f_{\text{HC}_2\text{O}_4^-}f_{\text{Cl}^-}$, which was evaluated for a range of ionic strengths by Pinching and Bates³ in the potentiometric determination of the ionization constants of oxalic acid. A reiterative calculation was utilized in which values of Γ_1 were estimated for the two titrations at different concentrations. From these quantities the K_1 and K_2 were evaluated by the use of equation 8 which then permitted an improved estimate of the ionic strength, etc.

Results and Discussion

The equilibrium constants, K_1 and K_2 , which were calculated from two titrations of solutions

(3) G. O. Pinching and R. G. Bates, *J. Research Natl. Bur. Standards*, **40**, 405 (1948).

with no added salt, are given in Table I. The constants K'_1 and K'_2 for an ionic strength of 0.318 were evaluated from two titrations of solutions containing NaNO_3 . The values of these equilibrium constants for 25° are given in Table I. The titers have been calculated from these equilibrium constants for the experiments other than the ones used in the equilibrium constant determination. These calculated titers are included in Table I. The agreement between observed and calculated titers is satisfactory, and over the limited concentration range studied no need for including a third acid hydrolysis was indicated. Also calculated were the relative concentrations of the individual species in each of the solutions listed in Table I.

The equilibrium constants in Table I indicate that at 25° the predominant species over the entire range studied was $[\text{PtCl}_3(\text{H}_2\text{O})]^{-}$. The fraction of total platinum in this form attains a maximum value of about 70% in 5×10^{-3} molar solutions. The $[\text{PtCl}_2(\text{H}_2\text{O})_2]$, which amounts to 41% and 28% for low ionic strength and for $\mu = 0.318$, respectively, in 1×10^{-3} molar solution, falls to less than 5% at 20×10^{-3} mole/l.

In repeated titrations and analyses, agreement of the significant T/a ratio was usually within 2%, although occasionally a deviation as high as 4% was obtained. A difference as high as 4% in one of the titers can change the calculated equilibrium constants, pK_1 by 0.06 unit and pK_2 by 0.24 unit. These quantities probably represent upper limits to the uncertainty, but they are sufficiently high so that attempts to evaluate ΔH^0 from the temperature coefficients will be unsatisfactory. Some exploratory experiments at 15° have indicated that ΔH^0 for each hydrolysis reaction is fairly small, *i.e.*, less than 10 kcal.

The equilibrium constants for reactions 1 and 2 indicated the presence of significant quantities of the uncharged species, $[\text{PtCl}_2(\text{H}_2\text{O})_2]$. The ion exchange experiments, described in the Experimental section, were designed to establish its presence. Our experience with platinum complexes has shown that an ion exchange column very effectively removes the properly charged species from solution. Some reduction of platinum usually occurs in the column and recovery of an uncharged species or an oppositely charged ion is sometimes not quantitative. Also, an ion retained by the resin can never be completely stripped from the column. For the solution with no added salt there was found in the effluent 9.3 mg. of Pt or nearly 60% of the element calculated to be present as $[\text{PtCl}_2(\text{H}_2\text{O})_2]$ from the initial concentration and K_1 and K_2 . In addition, the ratio of titer : platinum was 1.7 ± 0.3 which was consistent with the hypotheses. The results were less satisfactory for the sodium nitrate solution. However, the recovery amounted to 3.0 mg. Pt or 30% of the calculated quantity of $[\text{PtCl}_2(\text{H}_2\text{O})_2]$.

The difference between K_1 and K'_1 , corresponding to a lower degree of hydrolysis at higher ionic strengths, is very well in line with the expected dependence of the activity coefficient function Γ_1 upon ionic strength.³ However, no change with ionic strength is predicted for Γ_2 . Since the uncer-

tainties for K_2 and K'_2 are much larger than for K_1 and K'_1 , the observed rather large difference in the second hydrolysis constants may not be real. However, the ion exchange experiments were also consistent with a difference in the extent of the second hydrolysis.

A comparison of the $[\text{PtCl}_4]^-$ and $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]^-$ hydrolysis systems shows some very interesting similarities and differences. The $[\text{PtCl}_3(\text{NH}_3)]^-$ system was described in an earlier paper.⁴ K'_1 for the two systems are equal within experimental uncertainties. The presence of the NH_3 -ligand therefore cancels any electrostatic effect due to the differences in charge of the ions. However, for $[\text{PtCl}_4]^-$ the K_2 is at least ten times larger than for $[\text{PtCl}_3(\text{NH}_3)]^-$. For the latter system, the second hydrolysis reaction was not detectable by the dilution method which has been used in the present work.

The present experiments are in substantial agreement with the titrations which were performed only for aged 0.0166 M $K_2[\text{PtCl}_4]$ solutions in the original studies.^{2a} The analysis of the exchange kinetics is not changed significantly. However, in view of the extensive hydrolysis of the $[\text{PtCl}_3(\text{H}_2\text{O})]^-$, it appears that reaction 2 can account for the exchange of the chloride ligand of this complex with free chloride and that no additional process need be postulated.

An attempt has been made to estimate the dissociation constants for the three acids which were titrated in these experiments. A titration for solutions in NaNO_3 at $\mu = 0.318$ (substantially constant) was considered for which dissociation equilibrium constants were defined

$$[\text{PtCl}_3(\text{H}_2\text{O})]^-: K'_{11} = a_{\text{H}^+}[\text{PtCl}_3(\text{OH})^-]/[\text{PtCl}_3(\text{H}_2\text{O})]^- \quad (12)$$

$$[\text{PtCl}_2(\text{H}_2\text{O})_2]: K'_{21} = a_{\text{H}^+}[\text{PtCl}_2(\text{H}_2\text{O})(\text{OH})^-]/[\text{PtCl}_2(\text{H}_2\text{O})_2] \quad (13)$$

(4) T. S. Elleman, J. W. Reishus and D. S. Martin, Jr., *THIS JOURNAL*, **80**, 56 (1958).

$$[\text{PtCl}_2(\text{H}_2\text{O})(\text{OH})]^-: K'_{22} = a_{\text{H}^+}[\text{PtCl}_2(\text{OH})_2^-]/[\text{PtCl}_2(\text{H}_2\text{O})(\text{OH})]^- \quad (14)$$

a_{H^+} represents the hydrogen ion activity indicated by the pH meter. For a titration the starting concentrations of $[\text{PtCl}_3(\text{H}_2\text{O})]^-$ and $[\text{PtCl}_2(\text{H}_2\text{O})_2]$ were calculated from K'_1 , K'_2 and Pt-total. $E_{i\text{-obsd.}}$ were the equivalents of NaOH added to give pH_{*i*} for the *i*-th point on the titration curve. $E_{i\text{-calcd.}}$ can be computed from the concentrations of the two acids and a set of equilibrium constants K'_{11} , K'_{21} and K'_{22} . A program was processed on an IBM-650 computer to find the values of K'_{11} , K'_{21} and K'_{22} which minimized the sum of squares, $[(E_{i\text{-calcd.}} - E_{i\text{-obsd.}})/E_{i\text{-obsd.}}]^2$, for the titration points taken before the end-point. The computer was unable to select a set of constants satisfactorily for a high concentration solution, *i.e.*, $a = 0.0163$, in which the fraction y/a was only 0.03. However, for a solution of $a = 4.83 \times 10^{-3}$ for which $y/a = 0.09$ it selected values of $pK'_{11} = 7.0$, $pK'_{21} = 5.2$ and $pK'_{22} = 8.3$. From the results of different computations it is estimated that the uncertainty in pK'_{11} is less than 0.1 unit, but the uncertainty in pK'_{21} and pK'_{22} may be as high as 0.8 unit. These values for the dissociation constants appear reasonable in that the ionization constant of the neutral species $[\text{PtCl}_2(\text{H}_2\text{O})_2]$ is higher than that of the anion $[\text{PtCl}_3(\text{H}_2\text{O})]^-$. Also, there is a satisfactory, even if rather small, difference between the first and second ionization constants of $[\text{PtCl}_2(\text{H}_2\text{O})_2]$. The values of these dissociation constants are offered as tentative ones, however, until the computation method has been subjected to much more rigorous testing.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEXAS TECHNOLOGICAL COLLEGE, LUBBOCK, TEXAS]

The Chemistry of the Solvated Metal Chelates. IV. 8-Quinolinol Chelates of Scandium (III), Thorium (IV) and Uranium(VI)¹⁻³

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RECEIVED MAY 23, 1960

The 8-quinolinol metal chelates of scandium, thorium and uranium (VI) were studied by X-ray powder diagrams and non-aqueous titrations. X-Ray data showed that the solvated chelates were triclinic in structure while the unsolvated chelates were of monoclinic symmetry. The non-aqueous titrations of the solvated metal chelates with potassium methoxide in acetonitrile showed that the scandium and thorium compounds behaved in a different manner than the uranium compound. It was not possible to prepare "mixed chelates," where the solvate molecule was different than the coordinated groups.

Introduction

Of the many metals ions that form chelates with 8-quinolinol and its derivatives, only scandium (III), thorium (IV), uranium (VI) and plutonium

(VI) ions are known to form complexes of the type, $\text{M}(\text{C}_9\text{H}_6\text{NO})_n \cdot \text{C}_9\text{H}_6\text{NOH}$.⁴⁻⁷ All of these compounds contain an extra mole of chelating agent which is retained in the crystal, and in some

(1) Taken in part from the Ph.D. thesis of J. H. Van Tassel, Texas Technological College, August, 1959.

(2) Presented at the 15th Southwest Regional Meeting of the American Chemical Society, Baton Rouge, Louisiana, December 3-5, 1959.

(3) For part III see *J. Phys. Chem.*, **64**, 1289 (1960).

(4) L. Pokras and P. M. Bernays, *THIS JOURNAL*, **73**, 7 (1951).

(5) F. J. Prere, *ibid.*, **55**, 4362 (1933).

(6) P. Hecht and W. Reich-Rohrwig, *Monatsh. Chem.*, **53-54**, 596 (1929).

(7) R. G. Harvey, H. G. Heal, A. G. Maddock and E. L. Rowley, *J. Chem. Soc.*, 1010 (1947).