heat leak and the effect of small changes of temperature on the residual material. Correction also was made for the fact that the volume previously filled with liquid became available for gas. The values for ΔH were corrected to 298.15°K. over the small temperature range. The values are given in Table V.

The Entropy of Phosphoryl Chloride from the Calorimetric Data.—The entropy was calculated in the usual manner by graphical integration and a Debye extrapolation. The data are summarized in Table VI.

The microwave data of Williams, Sheridan and Gordy,[9] and the vibrational fundamentals as given by Ziomek, Piotrowsky and Walsh,[10,11] were used to calculate a statistical value of the entropy of $POCl_3$ gas.

Williams, Sheridan and Gordy found it necessary to combine their data with the electron diffraction data of Brockway and Beach[12] in order to obtain the moment of inertia about the symmetry axis

$I_1 = 422.3 \times 10^{-40}$ g. cm.^{2} molecule^{-1}

$I_2 = 419.2 \times 10^{-40}$

$I_3 = 578.7 \times 10^{-40}$

We have obtained the above values from a weighted average of the several isotopic species. $I_1 \neq I_2$ due to isotopic loss of symmetry.

Ziomek, Piotrowsky and Walsh calculate a value for the entropy at 298.16°K. as 77.38 gbs. mole^{-1}. This value must be in error since the experimental result, 77.75 gbs. mole^{-1}, is greater than the above value, whereas it must be equal or less than the value derived from quantum data. Ziomek, Piotrowsky and Walsh do not state which of the fundamentals were given a double weight. We have used their values for the fundamentals and the weights listed to bring the calorimetric and spectroscopic values into agreement. The fundamental frequencies in cm.$^{-1}$ are

$$\nu_1 = 1290,\ \nu_2 = 486,\ \nu_3 = 337,\ \nu_4 = 581(2),$$
$$\nu_5 = 267(2),\ \nu_6 = 193(2)$$

These give a value of 77.77 *vs.* the experimental value 77.75 gbs. mole^{-1}. These values do not include the contributions due to isotopic mixing or nuclear spin. The result of Ziomek, Piotrowsky and Walsh corresponds to a reversal of ν_3 and ν_5 with respect to the double weight.

The above data were used to calculate values for the thermodynamic properties of phosphoryl chloride gas. The thermodynamic properties for condensed phases and the gas are given in Tables VII and VIII, respectively.

We thank L. E. Murch for assistance with the experimental measurements, D. S. Thompson for assistance with some of the calculations and especially R. H. Valentine for much assistance throughout the entire research. We thank Professor W. D. Gwinn for consultation on the spectroscopic data of phosphoryl chloride.

BERKELEY, CALIFORNIA

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[9] Q. Williams, J. Sheridan and W. Gordy, *J. Chem. Phys.*, **20**, 164 (1952).

[10] J. S. Ziomek, E. A. Piotrowsky and E. N. Walsh, *Phys. Rev.*, **98**, 243 (1955).

[11] Technical Report 3, Office of Ordnance Research, Contract No. DA-11-022-ORD-1281 Project TB2-0001 (OOR No. 842), submitted June 8, 1954.

[12] L. O. Brockway and J. Y. Beach, THIS JOURNAL, **60**, 1836 (1938).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS, THE STATE UNIVERSITY]

Counterion Binding by Polyelectrolytes. V. The Effect of Binding of Univalent Cations by Polyphosphates on the Intrinsic Viscosity[1]

BY PHILIP D. ROSS AND ULRICH P. STRAUSS

RECEIVED AUGUST 7, 1959

The effect of alkali metal ions on the molecular dimensions of a long-chain polyphosphate has been determined by viscosity measurements at 0° in aqueous solutions maintained at 0.2 ionic strength with tetramethylammonium bromide. All alkali metal ions depress the intrinsic viscosity, but in different ways. It is shown that the intrinsic viscosity is not a unique function of either the degree of ionization of the polyphosphate or the degree of binding of the alkali metal ions. This result indicates the existence of specific solvent incompatibilities of site-bound ion-pairs. The previous explanation of the dependence of the binding constants for the association of the cations with PO_3^--groups on the cation concentration in terms of the molecular dimensions of the polymer chain has been confirmed.

One of the most characteristic and best known properties of polyelectrolytes is the strong dependence of their molecular dimensions on their degree of ionization.[2] More recently, phase separation and viscosity studies on long-chain polyphosphates have shown that the solvent incompatibilities of site-bound $LiPO_3$ and $NaPO_3$ groups were different and that such differences had a pronounced effect, comparable to that of the degree of ionization, on the molecular dimensions of the polyelectrolyte.[3] However, since the degree of binding of the Li^+ and Na^+ ions was not quantitatively known, the conclusions concerning the molecular dimensions were necessarily only qualitative. In the meantime, the binding of Li^+,

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[1] The contents of this paper are contained in a thesis to be submitted by P. D. Ross to the Graduate School of Rutgers, The State University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(30-1)1018.

[2] R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.*, **3**, 246 (1948); *Ann. N. Y. Acad. Sci.*, **51**, 836 (1949).

[3] U. P. Strauss, D. Woodside and P. Wineman, *J. Phys. Chem.*, **61** 1353 (1957).

Na^+, K^+, Cs^+ and tetramethylammonium (TMA^+) ions by polyphosphates has been measured by electrical transport and by dialysis methods.[4-6] Thus it is now possible to compare the effects of the above counterions on the molecular dimensions at corresponding degrees of binding, at corresponding degrees of ionization and at the same total ionic strength. This paper describes the results of an investigation in which the intrinsic viscosity of a long-chain polyphosphate was determined at 0° in alkali metal–tetramethylammonium bromide mixtures maintained at 0.2 ionic strength.

Such an investigation also was found useful for the following two reasons. First, it allowed for a test of certain assumptions made in a previous paper in this series[5] concerning the effect of the molecular dimensions on the binding constants for the association of cations with PO_3^--groups. Second, a rational method was developed for preparing solutions to yield linear plots of the reduced viscosity against polymer concentration. Such plots have been found to be curved and difficult to extrapolate if the solvent composition is held constant as the polymer concentration is varied.[7] By preparing solutions of different polymer concentrations which would be in membrane equilibrium with the same solvent mixture, utilizing previously obtained membrane equilibrium data,[6] the desired linearity was obtained.[8]

Experimental

Materials.—Tetramethylammonium polyphosphate (our sample No. TMAPP-R1) was prepared by ion-exchange from potassium *Kurrol's salt*.[9] The sample contained 13% water which remained after freeze-drying. Its weight-average degree of polymerization, P_w, was determined to be 2100 by viscosity measurements in 0.35 *N* NaBr. By storing the sample at −15°, degradation by the unremoved water was avoided, and the P_w was found to remain constant throughout the investigation.

Preparation of Solutions.—Solutions for determining the intrinsic viscosity of TMAPP in a solvent mixture, being (M^+) normal in alkali metal bromide and $[0.2 - (M^+)]$ normal in TMABr, were prepared by first dissolving the desired amounts of polymer in this solvent mixture. Then, depending on *W*, the weight of dissolved polymer, *b* ml. of a 0.2 *N* MBr solution was added. The quantity *b* was calculated by the relation

$$b = \frac{1000 \times W \times \beta_{MD}}{153[0.2 - (M^+)]} \qquad (1)$$

where β_{MD} is the fraction of PO_3^--groups neutralized by bound M^+ as determined by membrane equilibrium,[6] and 153 is the equivalent weight of the polymer. In this way, a solution containing polymer has these normalities: (PO_3^-) for the polymer, $(M^+) + \beta_{MD}(PO_3^-)$ for the alkali metal bromide and $0.2 - (M^+) - \beta_{MD}(PO_3^-)$ for TMABr.[10]

At the higher alkali metal ion concentrations, where no membrane equilibrium data are available, β_{MD} was estimated from graphs of β_{MD} against (M^+), with β_{MD} in the 0.2 *N* MBr solutions assumed to be equal to $1 - i$, interpolated from the membrane equilibrium data of Strauss and Ander.[11] In the 0.2 *N* MBr solutions, the reduced viscosity curves were linear without the addition of any excess MBr.

The solutions were refrigerated until used, and all measurements were completed within 3 hr. after the solutions were prepared. In all cases, the *p*H was maintained between 6.8 and 7.5. In several test runs, it was found that the viscosity remained constant for at least 5 hr., showing the absence of degradation.

Viscosity.—Viscosities were measured at 0.0° in a Bingham viscometer[12] operating at driving pressures from 30 to 200 g./cm.². Viscometer calibrations were made with sucrose solutions according to the method of Fuoss and Cathers.[13] Shear effects which in some cases amounted to from 5 to 10% of the reduced viscosity were eliminated by extrapolation to zero rate of flow. The over-all uncertainty in the intrinsic viscosity is estimated to be between 0.01 and 0.02 dl./g.

Results and Discussion

Intrinsic Viscosity and Degree of Binding.—The effect of the alkali metal ions on the intrinsic viscosity, $[\eta]$, of the polyphosphate is shown in Fig. 1 as a function of the normality of the alkali metal ions, (M^+). The TMA^+ normality of each solution was $0.2 - (M^+)$, so that the total ionic strength was constant at 0.2. Bromide was the by-ion. The values of $[\eta]$ which are a measure of the molecular dimensions are seen to decrease with increasing (M^+), but in a different way with each alkali metal ion. Thus, while lithium ion has the strongest depressing effect at very low (M^+), it has the least effect when $(M^+) = 0.2$. The values of $[\eta]$ for Li^+, Na^+ and K^+ when $(M^+) = 0.2$ are in the same order as previously observed for another TMAPP sample.[3] One might expect that the intrinsic viscosity would be determined by the binding of the alkali metal ions, and therefore in Fig. 2, $[\eta]$ is represented as a function of β_M, the fraction of PO_3^--groups neutralized by bound alkali metal ions as determined by electrophoresis.[5] It is seen that the effects of the alkali metal ions on $[\eta]$ are quite different. It is important to bear in mind that since both β_M and the degree of ionization, *i*, of the polyphosphate were derived from the same electrophoretic mobility data alone,[5] similar differences between the effects of the alkali metal ions also would have appeared if $[\eta]$ had been presented as a function of *i*. Thus, the molecular dimensions are not uniquely determined by either *i* or β_M. These data represent conclusive confirmation for the previously reported specific solvent incompatibilities of associated MPO_3-groups.[3] This difference in solvent incompatibilities is also reflected in the second virial coefficients obtained by light scattering,[14] in phase separation experiments with polyphosphates[3] and polyvinylsulfonates[15] and in viscosity results obtained with sodium polyacrylate.[16]

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[4] U. P. Strauss and S. Bluestone, THIS JOURNAL, **81**, 5292 (1959).

[5] U. P. Strauss and P. D. Ross, *ibid.*, **81**, 5295 (1959).

[6] U. P. Strauss and P. D. Ross, *ibid.*, **81**, 5299 (1959).

[7] P. D. Ross, unpublished results.

[8] This method was suggested previously for a solvent containing a single simple electrolyte [U. P. Strauss, *J. Polymer Sci.*, **33**, 291 (1958)]. Earlier, linear reduced viscosity plots were obtained by a trial and error procedure [H. Terayama and F. T. Wall, *ibid.*, **16**, 357 (1955)].

[9] R. K. Iler, *J. Phys. Chem.*, **56**, 1086 (1952).

[10] Such a solution has an alkali metal bromide concentration which is in membrane equilibrium with that of the original solvent mixture in which the intrinsic viscosity is to be determined. To a very close approximation, the same can also be said about the TMABr concentration. The excess MBr takes care of the preferential binding of M^+ over TMA^+ by the polyphosphate.

[11] U. P. Strauss and P. Ander, THIS JOURNAL, **80**, 6494 (1958).

[12] E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, N. Y., 1922.

[13] R. M. Fuoss and G. I. Cathers, *J. Polymer Sci.*, **4**, 97 (1949).

[14] U. P. Strauss and P. L. Wineman, THIS JOURNAL, **80**, 2366 (1958); U. P. Strauss and P. Ander, unpublished results for the system $LiPO_3$-LiBr-H_2O.

[15] H. Eisenberg and G. R. Mohan, *J. Phys. Chem.*, **63**, 671 (1959).

[16] I. Kagawa and R. M. Fuoss, *J. Polymer Sci.*, **18**, 535 (1955).

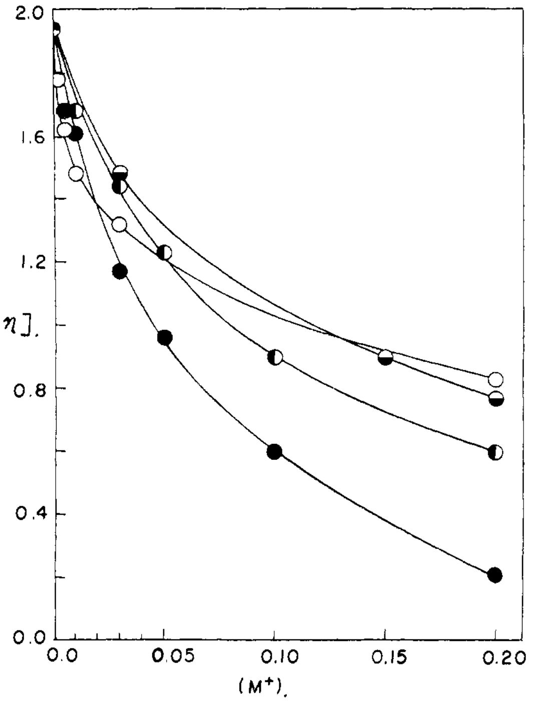

Fig. 1.—The intrinsic viscosity as a function of the alkali metal ion concentration at 0.2 ionic strength: ○, Li^+; ●, Na^+; ◐, K^+; ◒, Cs^+; ◓, TMA^+ without added alkali metal ion.

In order to discuss this phenomenon somewhat further, let us treat first the case of Li^+ and Na^+, where the values of β_M have been independently confirmed by membrane equilibrium measurements.[6] It has been suggested in one of the previous papers of this series[5] that the specific interactions may be caused by one cation bridging two PO_3^--groups situated in different portions of the polymer chain. The insensitivity of the binding constant K_{Li} for the association between Li^+ and a PO_3^--group to the molecular dimensions suggested that the bridging effect was insignificant for the lithium ion, presumably because the anhydrous Li^+ is too small to produce such an effect.[5] The increase of K_{Na} with decreasing molecular dimensions, on the other hand, was taken as evidence for such a bridging effect.[5] The curves in Fig. 2 support this conclusion. Thus, to a first approximation, one may consider the decrease of $[\eta]$ with increasing (Li^+) as being due mainly to a decrease in the degree of ionization of the polyelectrolyte. The distance between the Li^+ and Na^+ curves may then be ascribed to the bridging effect of Na^+.

With K^+ and Cs^+, the situation is more complex. In contrast to the behavior of Li^+ and Na^+, it was previously observed that the membrane equilibrium values of β_M[6] were much higher than the electrophoresis values used here. Adhering to our tentative interpretation that the electrophoresis values represent the site-bound M^+ ions while the dialysis values also include those K^+ or Cs^+ ions which are preferentially contained in the ionic atmosphere[17] around the polymer chain, the results

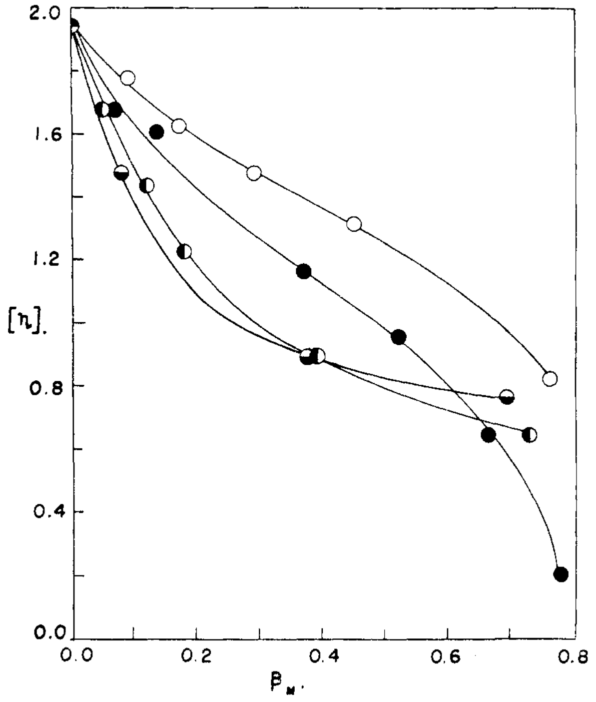

Fig. 2.—The effect of the binding of alkali metal ions on the intrinsic viscosity: ○, Li^+; ●, Na^+; ◐, K^+; ◒, Cs^+; ◓, TMA^+ without added alkali metal ion. The value of β_M for the next to the lowest point on the Na^+-curve was interpolated from a β_M against (Na^+) plot.

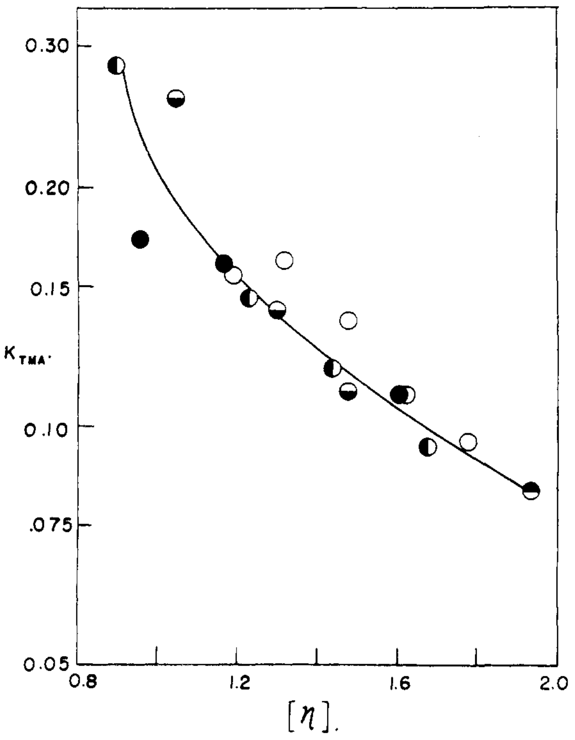

Fig. 3.—Test plot of K_{TMA} as a function of the molecular dimensions, added alkali metal ions: ○ Li^+; ●, Na^+; ◐, K^+; ◒, Cs^+; ◓, none. For the first Li^+-point and the first two Cs^+-points, $[\eta]$ was interpolated from Fig. 1.

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[17] For a detailed explanation see reference 6.

in Fig. 2 are very likely affected by such double-layer binding. Since with the smaller hydrated cations a greater number of cations can be accommodated in the ionic atmosphere, the enhanced electrostatic shielding effect would be expected to contribute to the contraction of the polymer coil. It is noteworthy that, if the intrinsic viscosity is plotted against the β_{MD}-values obtained from dialysis measurements, the curves for K^+ and Cs^+ lie quite close to the curve for Li^+. Unfortunately, since we do not know how to separate the effects of double-layer binding and of ion-bridging on $[\eta]$, these results do not supply any additional information concerning the ion-bridging of K^+ and Cs^+, which was postulated previously on the basis of other evidence.[5]

Molecular Dimensions and Binding Constants.—The previously mentioned explanation of the observed increase in the binding constant between a cation and a PO_3^--group with increasing (M^+) in terms of a contraction of the polymer coil[5] is tested in Fig. 3 where K_{TMA}[5] is presented as a function of $[\eta]$. It is seen that, to a first approximation, K_{TMA} is a function of $[\eta]$ alone, regardless of which alkali metal ion is employed. This result is consistent with and strongly supports the preceding explanation.

NEW BRUNSWICK, N. J.

[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, THE UNIVERSITY OF CHICAGO]

Molecular Complexes and their Spectra. XI. The Interaction of Iodide with Tri-*n*-Butyl Phosphate[1]

BY HIROSHI TSUBOMURA[2] AND JONATHAN M. KLIEGMAN

RECEIVED SEPTEMBER 18, 1959

The interaction between iodine and tri-*n*-butyl phosphate (tBP) has been studied spectroscopically. The visible iodine band in *n*-heptane solution shifts from 525 to 450 mμ as a result of the complexing with tBP. From quantitative measurements of the intensity of the shifted iodine band at various concentrations and temperatures, it has been found that iodine and tBP form stable 1:1 complex, with ΔH of −2.94 kcal./mole and ΔS of −3.99 e.u. The ΔH value obtained is intermediate between those for the iodine complexes with ether and ethanol. Using perfluorohydrocarbon as a solvent, an absorption tail has been found for the complex at about 220 mμ, which is considered to be a part of the charge-transfer band of this complex with its peak lying at a shorter wave length. Taking into account the electronic structure of tBP, it is concluded that iodine interacts mainly with the oxygen atom which is directly bonded with the phosphorus atom. It has also been found that tBP does not interact specifically with π-acceptors such as *p*-quinone and tri-nitrobenzene.

Introduction

It has been found that tri-*n*-butyl phosphate (tBP) can extract nitric or hydrochloric acid from their aqueous solutions. Tuck[3] suggested the formation of a complex such as $(RO)_3P{=}O{-}HNO_3$. These results seem to indicate that tBP may have a fairly strong affinity toward such Lewis acids as iodine. In this paper, the interaction between iodine and tBP is studied by the spectrophotometric method.

Experimental

The purification of iodine and *n*-heptane was described elsewhere.[4] The tBP used was a Fisher Purified Reagent; its refractive index was found to be $n^{20}D$ 1.42486, very close to the literature value (1.42496). However, the *n*-heptane solution of this substance and iodine showed two time-dependent absorption bands in the near ultraviolet region, which later were found to be caused by a small amount of impurities. Distillation of tBP at 9 mm. leads to a slight decomposition, but distillation at 1 mm. was carried out without decomposition (b.p., 99°). The *n*-heptane solution of this distilled substance and iodine showed absorption spectra in the visible and ultraviolet region which did not change with time for at least one day. The *p*-quinone and the tri-nitrobenzene were Eastman Pure Organic Chemicals, the former being further purified by sublimation. The tri-*n*-butyl phosphite used was the "Practical" grade of the Eastman Organic Chemicals, further purified by distillation at 5 mm. with a b.p. of 104°. The perfluorohydrocarbon was given to our Laboratory several years ago by the Minnesota Mining and Manufacturing Co. It has a boiling region from 80° to 104°. Its infrared spectrum is similar to that of perfluoroheptane. Therefore, this material is considered to be a mixture of perfluorohydrocarbons, with the number of carbon atoms lying between 7 and 8. This material has ultraviolet absorption beginning at 300 mμ but can be purified by passing it through a column of silica gel, until no absorption band is found in the region above 220 mμ.

The visible and ultraviolet absorption spectra were measured with a Spectracord. A thermostated cell holder described in the previous paper[4] was used to maintain the temperature of the cell constant.

Results and Discussion

Visible Absorption Spectra.—The visible absorption spectra of the *n*-heptane solutions of iodine and tBP are shown in Fig. 1; tBP has no absorption in this range. It can be seen that a complex is formed between iodine and tBP, a new absorption band appearing with a peak at 460 mμ, which is most reasonably assigned to the visible iodine band shifted by complex formation. The corresponding free iodine band has its peak at 525 mμ.

Assuming a 1:1 association equilibrium, the equilibrium constant has been calculated from the intensities of the spectra of various solutions at 450 mμ. The wave length 450 mμ was chosen because the ratio of the intensity of the complexed to the free iodine band is the largest at that wave length. The determination of the equilibrium constant in this case is complicated owing to the superposition of the free iodine band with that of the complexed iodine. The method adopted

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[1] This work was assisted by a grant from the National Science Foundation.

[2] On leave of absence from the Institute for Solid State Physics, The University of Tokyo, Tokyo, Japan.

[3] D. G. Tuck, *J. Chem. Soc.*, 2783 (1958).

[4] H. Tsubomura, THIS JOURNAL, **82**, 40 (1960).