Electric Conduction and Density of Condensed Phosphoric Acids and Their Mixtures with Sulfuric Acid

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The electrolytic conductivities and densities of condensed phosphoric acids have been measured in the P_2O_5 concentration range from 55% to 80% at 55.0, 70.0, and 90.0°C. Assuming the proton jump mechanism through the hydrogen bond network of H_2O and H_3PO_4, the molar conductance was calculated and found to be constant in the P_2O_5 concentration range between 60% and 76%. The investigation has been extended to the mixtures of condensed phosphoric acids and concentrated sulfuric acid. The complex formation of $[H_4PO_4^+ \cdot HSO_4^-]$ and $[H_3O^+ \cdot HSO_4^-]$ has been suggested in the mixture.

The physical and chemical characteristics of condensed phosphoric acid (abbreviated as CPA) have been studied by a number of investigators.[1] However, the mechanism of the electric conduction in CPA still remains unclarified. The conduction should be closely related to the physico-chemical structure of CPA. This paper deals with the relation between the electric conduction and physico-chemical structure of CPA in relation concentrated sulfuric acid and its mixtures with CPA.

Studies have been made on the density[2-6] and electric conduction[7,8] of CPA, but the results do not coincide. The discrepancy can be ascribed to the difference in experimental procedures. Since the chemical composition and purity of an electrolyte affect density and conduction, the so-called "reorganization" of CPA[9] cannot be overlooked. The effect of reorganization of CPA on density and electrolytic conductivity has not so far been investigated except for anhydrous orthophosphoric acid[14,16] and we have therefore, examined it first. The measurements of electrolytic conductivity and density were undertaken over a wide range of P_2O_5 concentrations.

Some interesting information on the relation between the physico-chemical structure and electric conduction of CPA has been obtained by means of the concept of "molar conductance."

Experimental

The two conductivity cells used in this work were the same type as the one designed by Jones for precision measurements.[12] The electrodes were flat platinum disks (15 mm in diameter) not platinized, since a platinized platinum electrode undergoes corrosion in CPA. The cell constants were 4.72 and 11.97 cm^{-1}. The cell was placed in a constant temperature bath containing silicone oil. The measurements were carried out at 55, 70, and 90°C ±0.02°C. The curve, linear extrapolation to the infinite frequency of the measured resistance *versus* (frequency)$^{1/2}$, was constructed. The resistance at the infinite frequency can be considered to be free from impedance caused by electrode reactions.

The density measurement was carried out by weighing a calibrated silica cylinder (11.6 mm in diameter and 57 mm in length). The silica cylinder was suspended with a thin platinum wire from one end of an analytical balance and submerged in a liquid to be tested.

CPA was prepared as follows.

(1) Reagent grade phosphorus pentoxide was sublimated in iron pipes[10] in an oxygen atmosphere at 800°C in order to remove organic impurities and lower phosphorus oxides such as PO_2, P_2O_3, and P_4O_6.

(2) The purified P_2O_5 was then dissolved in reagent grade phosphoric acid by heating in a glassy carbon beaker.

(3) The concentration of CPA was determined by means of potentiometric titration.[11]

Results

Crystalline orthophosphoric acid is regarded to be H_3PO_4.[13] Upon fusion, a small portion of H_3PO_4 is converted into pyrophosphoric acid by self-dehydration and a part becomes triphosphoric acid. This process is called reorganization. The reorganization of orthophosphoric acid has been found to be accompanied by a decrease in conductance.[14] Crystalline phosphoric acid prepared by fractional freezing method[15] was reexamined first. It was melted just before the experiment and the conductivity was measured at 55, 70, and 90°C as a function of time. The conductivity decreased with time and reached a steady value, which can be considered to be the conductivity of the equilibrated mixture of $H_{n+2}P_nO_{3n+1}$ ($n=0, 1, 2, \cdots$). The time required to reach the equilibrated CPA was about one hour at 90°C and about 30 hours at 55°C.

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[1] J. R. Van Wazer, "Phosphorus and its Compounds," (Intersceince Pub. Inc., New York), Vol. 1, chap. 12 (1958). p. 717.

[2] J. H. Lum, J. E. Malowan, and C. B. Durgin, *Chem. and Met. Eng.*, **44**, 726 (1937).

[3] M. M. Striplin, D. Mcknight, and G. H. Megar, *Agricult. and Food Chem.*, **6**, 298 (1958).

[4] E. J. Griffith, Ref. 1, p. 771.

[5] D. E. Person and R. M. Stone, *J. Amer. Chem. Soc.*, **83**, 1715 (1961).

[6] S. Ohashi and H. Sugatani, This Bulletin, **33**, 1286 (1960).

[7] G. P. Kakoolin and I. G. Fedorrchenko, *Zhur. Neorg. Khim.*, **7**, 2485 (1962).

[8] I. G. Fedorrchenko, G. P. Kakoolin, and Z. V. Kondratchenko, *ibid.*, **10**, 1945 (1965).

[9] J. R. Van Wazer, Ref. 1, p. 747.

[10] G. I. Finch and R. Fraser, *J. Chem. Soc.*, **129**, 117 (1926).

[11] L. M. Kolthoff and P. J. Elving, "Treatise on Analytical Chemistry," Vol. 5, Interscience Pub. Inc., New York (1961), Part 2, p. 346,

[12] G. Jones and G. M. Bollinger., *J. Amer. Chem. Soc.*, **53**, 1207 (1931).

[13] A. Simon and G. Schulze, *Z. Anorg. Allgem. Chem.*, **242**, 313 (1939).

[14] R. A. Manson, *J. Phys. Chem.*, **69**, 1761 (1965).

[15] A. Simon and M. Weist, *ibid.*, **268**, 302 (1952).

The rate of self-hydration or dehydration is so high at a high temperature that CPA heat-treated at 200°C for one hour can be regarded as an equilibrated mixture of $H_{n+2}P_nO_{3n+1}$ ($n=0$, 1, 2, $\cdots$). The mixture was quenched in to a refrigerator and transferred into the conductivity cell. The conductivity of quenched CPA was then measured as a function of time at 55, 70, and 90°C. No change in the conductance was observed, that is, no change in the composition of CPA could be detected. It might be assumed from the result that the equilibrium constants of the self-hydration and dehydration reactions in a CPA were independent of temperature within experimental accuracy. All CPA's used in the following experiments were heat treated at 200°C for one hour.

The electrolytic conductivities *versus* P_2O_5 concentration are shown in Fig. 1. The conductivity decayed linearly with increasing concentration down to about 72% and then a rapid decrease was observed. The P_2O_5 concentration of 72% corresponds to the stoichiometrically pure orthophosphoric acid. This result coincides with those reported by other workers.8,6)

The densities *versus* P_2O_5 concentration are shown in Fig. 2. Tye results agreed with those reported by Ferr.4)

CPA can be considered to be a mixture of H_2O, H_3PO_4 $H_4P_2O_7$,$\cdots$$H_{n+2}P_nO_{3n+1}$ in the concentration range used in this experiment. In order to introduce the concept of "molar conductance," it was assumed first that the main conducting components in the CPA are H_2O and H_3PO_4 and that both H_2O and H_3PO_4 behave as equally effective species for the electric conduction of CPA. The molar conductance (Λ) of CPA, therefore, can be calculated from electrolytic conductivity (κ) and the density (ρ) by means of the following equation:

$$\Lambda = \kappa\sum\chi_i M_i/\rho(\chi_{H_2O}+\chi_{H_3PO_4}) \qquad (1)$$

where χ_i is the mole fraction of the ith component of the molecular weight of M_i and χ_{H_2O} and $\chi_{H_3PO_4}$ are the

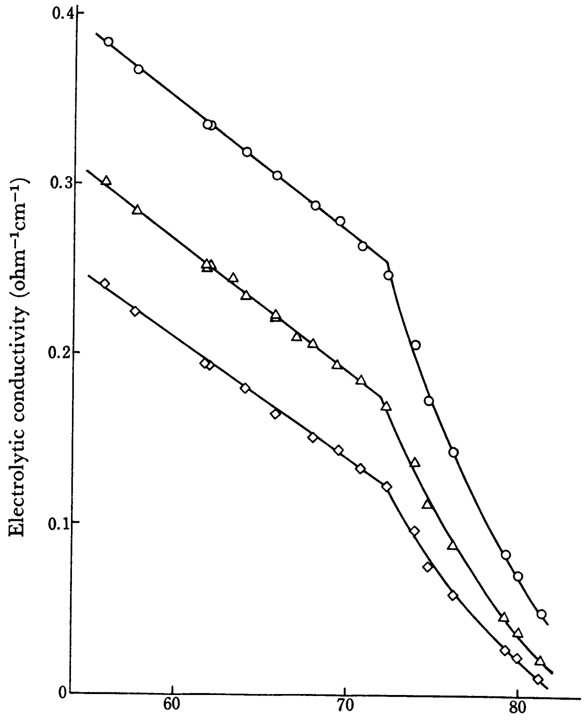

Fig. 1. Electrolytic conductivity of CPA.
Temp: 55°C (◇), 70°C (△), and 90°C (○).

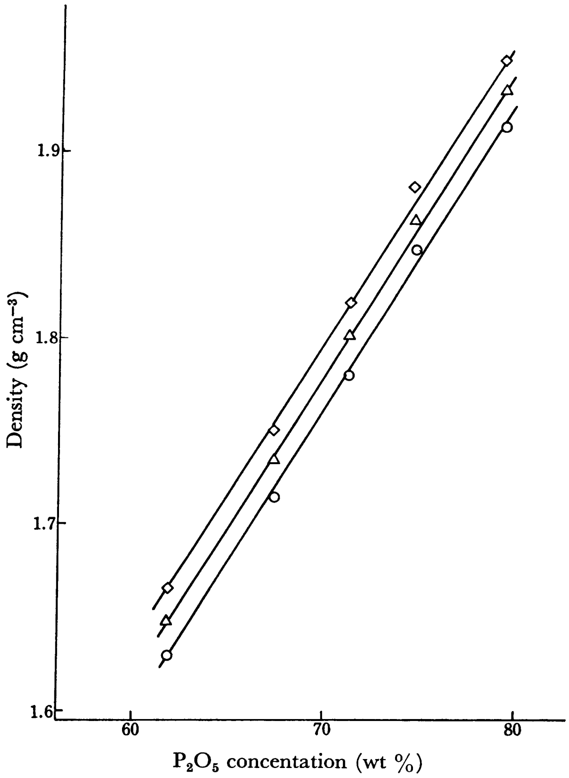

Fig. 2. Density of CPA. Temp.: 55°C (◇), 70°C (△), and 90°C (○).

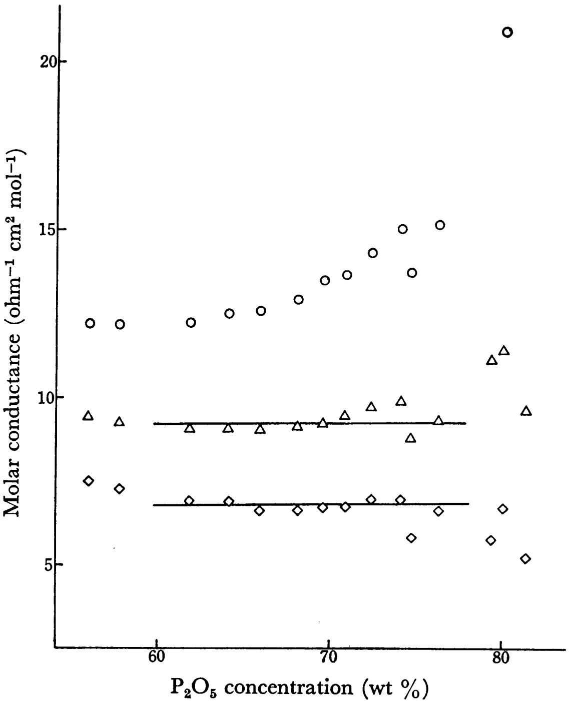

Fig. 3. Molar conductance of CPA.
Temp: 55°C (◇), 70°C (△), and 90°C (○).

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16) N. N. Greenwood and A. Thompson, *J. Chem. Soc.*, **1959**, 3485.

mole fractions of H_2O and H_3PO_4, respectively. They are given from the analytical data by Huhti and Gartaganis.[17] The calculated molar conductances are plotted against the P_2O_5 concentration in Fig. 3. It was noted that the molar conductances of CPA at 55 and 70°C are constant in the concentration range between 60% and 76%.

Concentrated sulfuric acid was mixed with CPA's of 61.8, 66.8, 70.8, 74.8, and 79.3%, respectively. The electrolytic conductivities of the five mixtures at 55°C are plotted in Fig. 4 against the weight percentages of CPA's, and the densities in Fig. 5. Measurements were carried out at 70 and 90°C. The results were very similar to those for 55°C. It was noted that the electrolytic conductivities of mixtures were far from additive as compared to those of CPA and H_2SO_4.

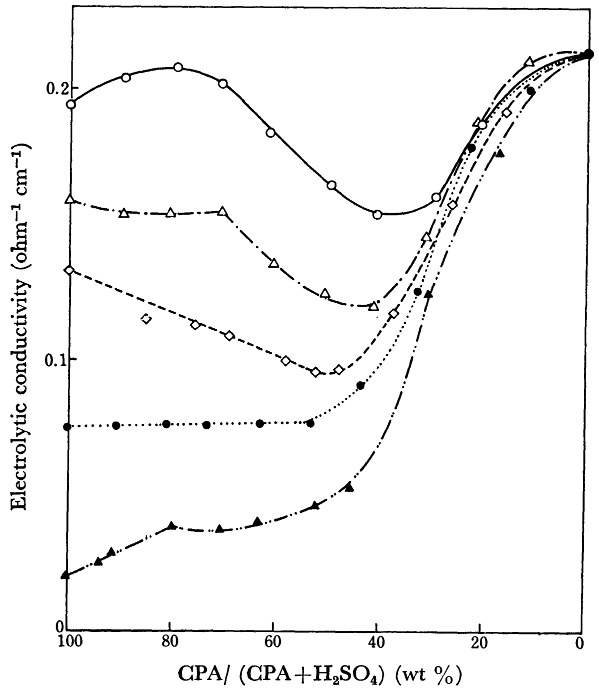

Fig. 4. Electrolytic conductivity of CPA-H_2SO_4 mixtures. 100% CPA's are of P_2O_5 concentrations of 61.8% (○), 66.8% (△), 70.8% (◇), 74.8% (●), and 79.3% (▲).

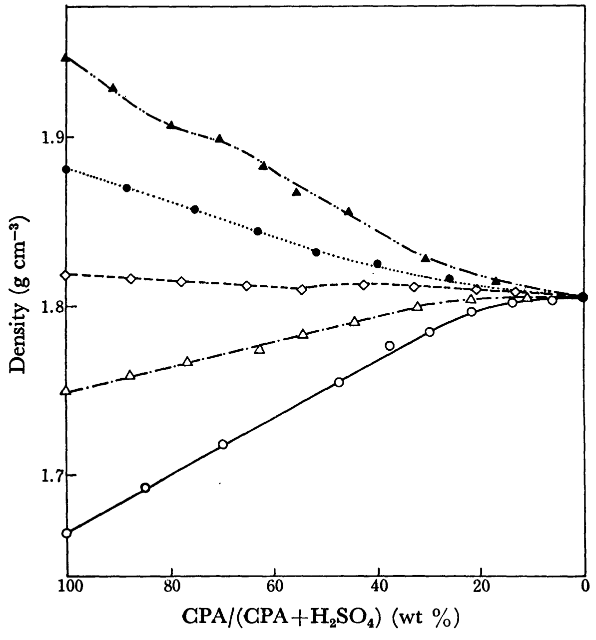

Fig. 5. Density of CPA-H_2SO_4 mixtures. Symbols are same as Fig. 4.

The molar conductance of CPA-H_2SO_4 mixture was introduced in a similar way to that of CPA. H_2O and H_3PO_4 as well as H_2SO_4 are assumed to be conducting components, and they behave as equally effective species on the electric conduction. Then, Eq. (1) becomes

$$\Lambda = \kappa \sum \chi_i M_i / \rho(\chi_{H_2O}+\chi_{H_3PO_4}+\chi_{H_2SO_4}) \qquad (2)$$

The molar conductances of mixtures at 55°C are plotted in Fig. 6 against the molar composition rate R which is represented by

$$R = (\chi_{H_2O}+\chi_{H_3PO_4})/(\chi_{H_2O}+\chi_{H_3PO_4}+\chi_{H_2SO_4}) \qquad (3)$$

The 79.3% CPA mixture was excluded in the figure since the discrepancy from the straight line in Fig. 3 was so remarkable that the assumption on the electric conduction of CPA does not hold for CPA of high P_2O_5 concentrations. It is particularly noteworthy in Fig. 6 that a minimum was observed at the R value of 0.5.

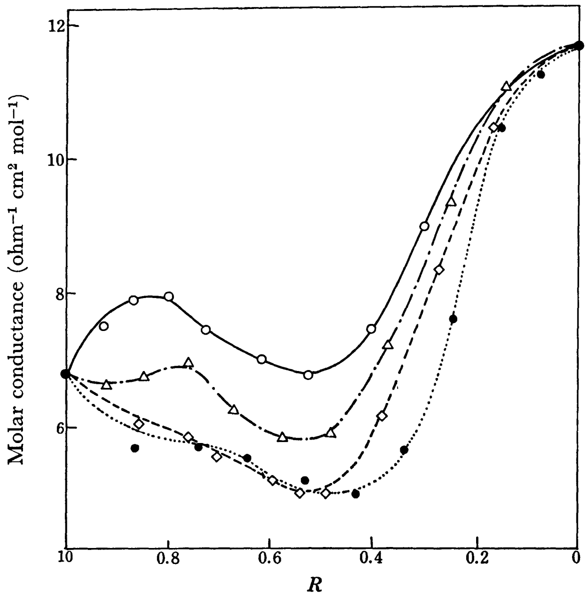

Fig. 6. Molar conductance of CPA-H_2SO_4 mixtures. Symbols are same as Fig. 4.

Discussion

CPA: The mechanism of electric conduction in condensed phosphoric acid as well as in anhydrous sulfuric acid has been investigated.[16,18] It was confirmed that the characteristic features of these acids are the self-dissociation into ionic products and their ability to conduct electricity by proton-jump. There are a number of ionic species in CPA such as H_3O^+,

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[17] A. L. Huhti and P. A. Gartaganis, *Can. J. Chem.*, **34**, 785 (1956).

[18] N. N. Greenwood and A. Thompson, *J. Chem. Soc.*, **1959**, 3475.

$H_4PO_4^+$, $H_2PO_4^-$, $H_3P_2O_7^-$. Greenwood and Thompson[16)] assumed that $H_2PO_4^-$ was the only conductive species with proton-jumps. They explained that the sharp drop in κ at about 72% P_2O_5 was due predominantly to the decrease in the concentration of anomalously conductive $H_2PO_4^-$ ions. All the previous discussions on the conduction mechanism of concentrated acids were based on an ion which has a high mobility by proton-switch conduction. In this investigation, however, the electrolytic conductivity and density data of CPA are handled on the basis of the length of hydrogen bond networks along which protons can be transferred; it was assumed that the hydrogen bond network leading to a high proton conductivity in CPA was constructed by H_2O and H_3PO_4. The "molar conductance" term which is defined by Eq. (1) has been introduced. When Λ was plotted against the cencentration of CPA, Λ at 55° and 70°C could be considered to be constant in the concentration range from 60% to 76% P_2O_5 (Fig. 3). This might indicated that our assumption of Eq. (1) is reasonable; the electric conduction of CPA (60%—76% P_2O_5) occurs by proton-jumps through the hydrogen bonds of H_2PO_4 and H_2O, and by the following rotation of these molecules. The constant value of Λ also seems to show that both H_2O and H_3PO_4 bahave as equally effective species on electrical conduction. Condensed phosphoric acids of higher molecular weights such as pyrophosphoric acid and triphosphoric acid do not play important roles in the conduction of CPA in this concentration range because the massiveness inhibits the rotation of molecule after a proton-jump. The discrepancy of Λ's from a streight line at 90°C can be attributed to the additional contribution of pyrophosphoric acid to the conduction, since it seems that the rotation of a massive molecule becomes more favorable at higher temperatures. The discrepancy of Λ's from straight lines at low P_2O_5 concentrations of CPA can be assumed to be due to the ionic conduction by hydrated H^+ and ionized phosphoric acids.

We assumed that H_2O as well as H_3PO_4 is electrical conductive species, whereas Greenwood *et al.*[16)] concluded that H_3O^+ could not be considered as conductive species since H_3O^+ was unlikely to take part in the hydrogen bonded structure of CPA. The conclusion by Greenwood was made by the analogy of the behavior of H_3O^+ in sulfuric acid. The structure of CPA, however, is considered to be a more complicated hydrogen bridge system containing mobile protons as current-carrying species. The Raman spectroscopy and other physico-chemical properties of anhydrous H_3PO_4 were studied by Simon and his co-workers.[13,15)] It was suggested that there are free mobile protons which are not located at a fixed PO_4 group. Mobile protons were also found within the hydrogen bonded structure of water and ice by Eigen and Mayer.[19)] It seems, therefore, to be reasonable to assume that H_2O is a conductive species in CPA.

It is interesting that the molar conductance of CPA does not depend upon the ratio of H_2O to H_3PO_4. This shows either that the number of mobile protons as well as mobility do not change with the change of the ratio of H_2O to H_3PO_4, or that the increase of mobility and the decrease of number mobile protons occur at the same rate with the change in the concentration of CPA. This is still an open question.

The reorganization rate of orthophosphoric acid could be calculated by use of the assumption. Suppose α mol% of orthophosphoric acid is converted into pyrophosphoric acid. The electrolytic conductivity of pure orthophosphoric acid (κ_0), which is the initial conductivity, changes to conductivity (κ_0) of the reorganized phosphoric acid mixture according to the equation

$$\kappa_e = \kappa_0(1-\alpha/100). \qquad (4)$$

The reorganization rate calculated by this equation was 6.6 mol% at 70°C, and coincided with 6.38 mol% obtained by means of paper chromatography.[17)]

CPA-H_2SO_4 Mixtures: The idea of the hydrogen bond network of H_2O and H_3PO_4 assumed for CPA is extended for CPA-H_2SO_4 mixtures. Upon calculation of the molar conductance for the mixtures, it was assumed that H_2SO_4 plays a part in the network of H_2O and H_3PO_4 as an equally effective species of conduction. Variation of the molar conductance in Fig. 6 show that the mixture is complicated. The complication also could be predicted from the that the electrolytic conductivity was far from the additivity of that of CPA and H_2SO_4. Reorganization of CPA by the addition of H_2SO_4 can not be neglected; however, in following discussion, the mole fractions of H_2O, H_3PO_4, and H_2SO_4 are calculated by assuming that no reorganization reaction of CPA occurs upon mixing with H_2SO_4. The most interesting result is that there exists a minimum in the molar conductance for R value of 0.5, where the molar ratio of $[H_2O+H_3PO_4]$ to $[H_2SO_4]$ was unity, as seen in Fig. 6. The minimum suggests the complex formation between H_3PO_4 and H_2SO_4 as well as between H_2O and H_2SO_4, such as $[H_4PO_4^+\cdot HSO_4^-]$ and $[H_3O^+\cdot HSO_4^-]$. It seems to be reasonable to assume such complex formation because H_2SO_4 has been found to be a strong mono-protonic acid in CPA.[20)] It can be concluded that the length of hydrogen bonding reduced by complex formation, resulting in a decrease in the molar conductance of pure CPA or pure H_2SO_4 by mixing.

The ionic conduction plays a role in the electric conduction of a CPA of low P_2O_5 concentration. The addition of H_2SO_4 into a CPA of low concentration caused the increase in the molar conductance up to the R value of 0.8. This can be explained by the increase of conductive ions by mixing H_2SO_4 with CPA of low concentration.

An inflection point exists in the electrolytic conductivity curve and the density curve at a high P_2O_5 concentration CPA of 79.3%. The weight % of CPA at the inflection was 80% for the electrolytic conductivity curve and 70% for the density curve. The mechanism of electric conduction in the pure CPA of 79.3% is still unknown.

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19) M. Eigen and L. D. Mayer, "Structure of Electrolytic Solutions," ed. W. J. Hamer, John Willy & Sons, Inc., New York, (1959), p. 64.

20) R. A. Munson, *J. Phys. Chem.*, **68**, 3374 (1964).