1693 cm.$^{-1}$ in H_2O solution, and 1709 cm.$^{-1}$ in concentrated HCl) in the acid solution. This same shift (to 1709 cm.$^{-1}$ in concentrated HCl) has been observed for the carbonyl frequency by Sannie and Poremski[17] in their study of the Raman spectrum of acetamide in concentrated HCl and indicates that acetamide also takes up a proton to form $CH_3CONH_3^+$ in concentrated HCl. This interpretation of the 1709 cm.$^{-1}$ band had already been made by Sannie and Poremski.[17] Our results show that the 1611 cm.$^{-1}$ band of acetamide[17] does not belong to ν(C–N) of the imino alcohol form of acetamide since the corresponding band in formamide disappears on deuteration.

[17] C. Sannie and V. Poremski, *Bull. soc. chim.*, **6**, 1629 (1939).

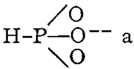
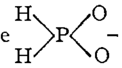
RUSTON, LOUISIANA

[CONTRIBUTION FROM THE RANDALL LABORATORY OF PHYSICS, UNIVERSITY OF MICHIGAN]

Vibrational Spectra of Phosphite and Hypophosphite Anions, and the Characteristic Frequencies of PO_3^{--} and PO_2^- Groups

BY MASAMICHI TSUBOI[1]

RECEIVED JULY 30, 1956

Infrared absorption spectra of the  $H\text{–}PO_3^{--}$ anion and Raman and infrared spectra of the  $H_2PO_2^-$ anion have been obtained in the solid state and in aqueous solution. All of the expected fundamental vibrations can be reasonably assigned to the observed bands. The PO_2^- symmetric and antisymmetric stretching vibrations in the $H_2PO_2^-$ anion occur at 1050 and 1200 cm.$^{-1}$, respectively. Similar bands are observed at almost the same frequencies for the $(CH_3O)_2PO_2^-$ anion and the Na-salts of nucleic acids. The PO_3^{--} symmetric and asymmetric (degenerate) stretching vibrations of the HPO_3^{--} anion give bands at 980 and 1100 cm.$^{-1}$. respectively. These vibrations in the $CH_3OPO_3^{--}$ anion and in nucleotides in solution at high *p*H seem to give bands at almost the same positions. These are considered to be characteristic frequencies of the PO_2^- and PO_3^{--} groups.

Introduction

Although accumulating infrared and Raman spectra cover a great variety of compounds, our knowledge of the vibrational spectra of simple phosphorus compounds is still quite limited. Several authors[2–4] have investigated the Raman spectra of phosphite and hypophosphite anions but so far no infrared data seem to be available. In spite of the simple structure of these anions, the assignment of their fundamental frequencies has never been complete. In view of this situation, the infrared absorption spectra of a few salts containing these anions have been investigated. The Raman spectrum of potassium hypophosphite has been reexamined, since previous data on the hypophosphite ion are not in agreement on some points. The results of this study have led to a reasonable assignment of the fundamental frequencies. It is shown that the knowledge thus obtained facilitates the interpretation of the vibrational spectra of other compounds with PO_3^{--} and PO_2^- groups.

Hypophosphite Anion and the PO_2^- Group.—The results of the Raman and infrared measurements for 50% aqueous solution of KH_2PO_2 are given in the first and the second columns of Table I. A thin sheet of solid KH_2PO_2 was prepared in which, fortunately, thin pyramidal crystals were oriented with their axes practically along one direction. It was thus possible to obtain infrared absorption data on solid KH_2PO_2 with polarized radiation. The results are given in the third column of Table I.

Previous authors have reported a Raman line for the $H_2PO_2^-$ ion at about 586 cm.$^{-1}$; it is weak according to Mathieu and Jacques[3] but it is stronger than the 467 cm.$^{-1}$ line according to Hanwick and Hoffman.[4] Hanwick and Hoffman[4] reported another line at 777 cm.$^{-1}$. In the present work, however, no appreciably intense lines could be found near these frequencies on plates which were properly exposed for the other lines. The strong band near 2350 cm.$^{-1}$ was always found to be accompanied by a weaker, depolarized line at 2311 cm.$^{-1}$ which was not reported by the previous authors.

TABLE I

VIBRATIONAL SPECTRA OF THE HYPOPHOSPHITE ANION[a]

Raman, cm.$^{-1}$ KH_2PO_2 aq. soln. (Int.)	(dep. rat.)	Infrared, cm.$^{-1}$ KH_2PO_2 aq. soln.	KH_2PO_2 crystal	Assignment
467 (5)	p(0.74)	469(m)	476(s)	A_1 PO_2 scissor
822 (1)	d?	811(s)	808(s) ‖	B_1 PH_2 rock
924 (7)	d(0.84)	.....	.....	A_2 PH_2 twist
1048(10)	p($\ll$0.5)	1042(s)	1046(s) ⊥	A_1 PO_2 sym. stretch
1088 (5)	d(0.94)	1086(m)	1080(w) ⊥	B_2 PH_2 wag
1157 (7)	p(0.71)	1160(s)	1171(s) ⊥	A_1 PH_2 scissor
.....		1180(s)	1230(s) ⊥	B_2 PO_2 anti. stretch
2311 (5)	d?	2314(s)	2312(s) ‖	B_1 PH_2 anti. stretch
2357(10)	p($\ll$0.5)	2363(w)	2375(m) ⊥	A_1 PH_2 sym. stretch

[a] s, strong; w, weak; m, medium; ‖, polarized parallel to the long crystal axis; ⊥, polarized perpendicular to the long crystal axis.

In the interpretation of the results, a non-planar structure with C_{2v} symmetry was assumed for the $H_2PO_2^-$ ion[5] (see Fig. 1). There should be nine normal vibrations, and the present assignment of these to the observed bands is given in the last column of Table I.

It is reasonable to take the lowest frequency (467 cm.$^{-1}$) for the PO_2 scissoring motion and the

---

[1] Fulbright Travel Grantee. Department of Chemistry, Faculty of Science, Tokyo University, Hongo, Tokyo, Japan.

[2] A. Simon and F. Feher, *Z. anorg. allgem. Chem.*, **230**, 289 (1937).

[3] J. P. Mathieu and J. Jacques, *Compt. rend.*, **215**, 346 (1942).

[4] T. J. Hanwick and P. O. Hoffman, *J. Chem. Phys.*, **17**, 1166 (1949); **19**, 708 (1951).

[5] W. H. Zachariasen and R. C. L. Mooney, *ibid.*, **2**, 34 (1934).

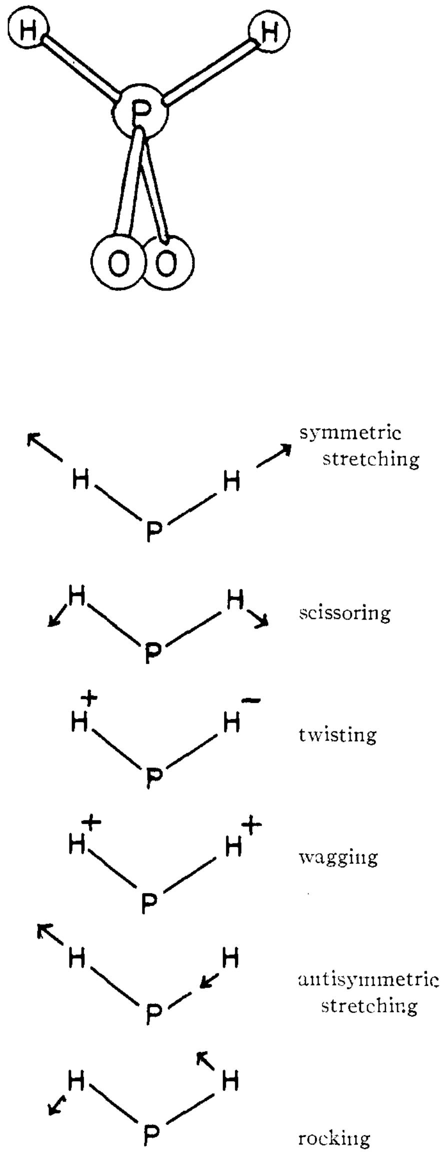


Fig. 1.—Structure of the H_2PO_2 ion and the PH_2 vibrations.

two highest frequencies (2357 and 2311 cm.$^{-1}$) for the two PH_2 stretching motions. Relative intensities of the PH_2 stretching bands in the Raman and infrared spectra and their depolarization ratios in the Raman spectrum suggest that the high frequency band arises from the PH_2 symmetric stretching vibration and the low frequency band from antisymmetric stretching vibration. It is interesting to note that the frequency relation here is the reverse of that found in the cases of CH_2, NH_2 and OH_2, where the antisymmetric stretching vibration always has a higher frequency than the symmetric vibration.

Of the remaining six bands, only the one at 808 cm.$^{-1}$ is found to have its transition moment in the same direction as that of the PH_2 antisymmetric stretching band (see the third column of Table I). Hence, this band must be attributed to the PH_2 rocking motion (see Fig. 1). The band at 924 cm.$^{-1}$ is very strong in the Raman spectrum, while it is completely absent in the infrared spectra. Therefore, this must be due to the PH_2 twisting motion, which is predicted to be Raman active but infrared inactive.

The assignment of the other four bands does not seem to be strictly unique at present. It is probable, however, that the band at 1048 cm.$^{-1}$, which is very strong in the Raman spectrum and is highly polarized, is due to the PO_2 symmetric stretching motion. The band at 1157 cm.$^{-1}$ is partially polarized and is therefore assigned to the PH_2 scissoring motion. The PH_2 wagging frequency can be assumed to be lower than the PH_2 scissoring frequency, and a relatively weak band at 1088 cm.$^{-1}$ is assigned to this mode. Finally, the strong absorption band at 1180 cm.$^{-1}$ is assigned to the PO_2 antisymmetric stretching vibration, although it is not clear why this frequency does not appear at all in the Raman spectrum. This band is located at a much higher frequency (1230 cm.$^{-1}$) in the crystal than in aqueous solution. This may be due to hydrogen bonding in aqueous solution between the O–H of water and the O of the PO_2^- group.

The crystal structure of ammonium hypophosphite was determined by Zachariasen and Mooney.[5] According to them, the $H_2PO_2^-$ anion has a non-planar structure with C_{2v} symmetry, and in the crystal (orthorhombic) the H–H line of every anion is directed along the *b*-axis. If the long axis of the KH_2PO_2 crystal is the *b*-axis and the anion is similarly oriented with respect to it, the PH_2 antisymmetric stretching motion and the PH_2 rocking motion would be expected to be polarized parallel to the long axis and all other fundamental bands should be polarized perpendicular to it. This is what was observed for the KH_2PO_2 crystal. Therefore, the infrared dichroism of the KH_2PO_2 crystal is consistent with its crystal structure being similar to that of $NH_4H_2PO_2$.

Incidentally, in crystalline $Ca(H_2PO_2)_2$, many bands associated with the anion split into two components. The splitting is particularly marked for the band assigned to the PO_2 symmetric stretching vibration (the separation of the components is 28 cm.$^{-1}$). The inactive band at 924 cm.$^{-1}$ appears in this crystal as a weak doublet.

Support of the above assignments for the $H_2PO_2^-$ anion is obtained from the infrared spectrum of the dimethyl phosphate anion, $(CH_3O)_2PO_2^-$. The Ba-salt of this anion gives a strong band at 1231 cm.$^{-1}$ in the crystalline state. This band shifts to a lower frequency in aqueous solution (to 1205 cm.$^{-1}$) just as did the 1230 cm.$^{-1}$ band in KH_2PO_2. Therefore, this band may be attributed to the PO_2^- group (antisymmetric stretching vibration) in both $H_2PO_2^-$ and $(CH_3O)_2PO_2^-$. Barium dimethyl phosphate also gives a strong band at 1054 cm.$^{-1}$. This is almost at the same frequency where the PO_2 symmetric stretching vibration of KH_2PO_2 is found. Thus, two strong bands at about 1050 and 1200 cm.$^{-1}$ may be considered to be characteristic bands of the PO_2^- group.

The Na-salts of nucleic acids contain many PO_2^- groups. Therefore, the above two characteristic frequencies (1050 and 1200 cm.$^{-1}$) may also expected in their spectra. Actually, both are found in sodium desoxyribonucleate and sodium ribonucleate.[6] In fact, the appearance of an isolated strong band in the 1220–1240 cm.$^{-1}$ region is one of the characteristic features of the infrared spectrum of the Na-salt of nucleic acid. It has been shown that this band cannot be assigned to the sugar or the base part of the nucleic acid structure.[7] It therefore is certainly due to the antisymmetric vibration of the PO_2^- group in the structure. It is interesting to note that this band, which is located at about 1240 cm.$^{-1}$ in dry Na-salts of nucleic acids, shifts to lower frequency (down to 1220 cm.$^{-1}$) when the nucleic acid salt adsorbs water, just as does the 1200 cm.$^{-1}$ band in $H_2PO_2^-$ and $(CH_3O)_2PO_2^-$ anions when they are dissolved in water.

Phosphite Anion and the PO_3^{--} Group.—Infrared spectra of an aqueous solution of potassium phosphite, K_2HPO_3, and of crystalline barium phosphite, $BaHPO_3$, in Nujol were examined.

The observed bands are listed in Table II, together with the Raman lines observed for an aqueous solution of Na_2HPO_3 by Mathieu and Jacques.[3]

TABLE II

VIBRATIONAL SPECTRA OF THE PHOSPHITE ANION[a]

Raman,[3] cm.$^{-1}$	Infrared, cm.$^{-1}$		
Na_2HPO_3 aq. soln.	K_2HPO_3 aq. soln.	$BaHPO_3$ cryst. in Nujol	Assignment
459(m) d	465(m) b	471(m) 498(m)	E PO_3 deg. def.
550(vw) ?	567(m)	591(m)	A_1 PO_3 sym. def.
993(s) p	979(m) sh	977(m) sh	A_1 PO_3 sym. str.
1032(m) d	1027(vw) b	1006(w) sh 1021(w) sh	E PH def.
1100(vw) ?	1085(vs) b	1083(vs) b 1110(vs) b	E PO_3 deg. def.
2330(s) p	2315(m) sh	2410(m) sh	A_1 PH str.

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; d, depolarized; p, polarized; b, broad; sh, sharp.

Assuming that the HPO_3^{--} ion has C_{3v} symmetry,[8] we may expect three bands due to totally symmetric vibrations and three bands due to doubly degenerate vibrations. As is shown in the table, six bands are observed in solution of which three split into two components each in the crystal. The splitting of a band in the crystalline state is not always due to the removal of degeneracy. In the case of crystalline $Ca(H_2PO_2)_2$, for example, the band due to the symmetric PO_2^- stretching vibration splits into two components probably as a result of intermolecular interaction, their separation being 28 cm.$^{-1}$ (see above). In the case of crystalline $BaHPO_3$, however, the splitting seems to be due to removal of the degeneracy.

The band near 2300 cm.$^{-1}$ is certainly attributed to the P–H stretching vibration. The Raman line at 993 cm.$^{-1}$ is strong and polarized. (The corresponding infrared band is very sharp both in solution and in the crystal.) This is almost undoubtedly due to the symmetric PO_3 stretching vibration. Of the two (degenerate) bands at 1100 and 1032 cm.$^{-1}$, the former is very strong and the latter is extremely weak in infrared absorption. Therefore it seems more probable that the former band arises from the degenerate PO_3 asymmetric stretching vibration and the latter from the PH deformation vibration than *vice versa*. This former assignment seems to be consistent with the fact that other compounds with the PO_3^{--} group show a strong band at 1100 cm.$^{-1}$ but none at 1032 cm.$^{-1}$. The two bands at 459 and 550 cm.$^{-1}$ must be due to PO_3 deformation vibrations. The band at 459 cm.$^{-1}$ is depolarized in the Raman spectrum and splits into two components in the crystal. Therefore, this is most probably assigned to the degenerate PO_3 asymmetric deformation. The other band must therefore be assigned to the PO_3 symmetric deformation vibration.

Thus, in the HPO_3^{--} anion the PO_3 symmetric and asymmetric stretching motions seem to give a sharp band at 980 cm.$^{-1}$ and a broad band at 1100 cm.$^{-1}$, respectively. An examination has been made as to whether these two bands may be considered as characteristic of the PO_3^{--} group.

Barium monomethyl phosphate, $BaCH_3OPO_3$, shows a sharp band at 985 cm.$^{-1}$ and a group of bands near 1100 cm.$^{-1}$ (consisting of two strong bands at 1121 and 1071 cm.$^{-1}$ and a shoulder at 1088 cm.$^{-1}$). The former is almost certainly due to the PO_3 symmetric vibration. The latter may be due essentially to the PO_3 asymmetric vibration, but ambiguity arises because of the expected splitting of the band due to the removal of the degeneracy, the expected superposition of the band due to the C–O stretching motion and the coupling with that motion and the PO_3 asymmetric stretching motion.

Nucleotides should take the PO_3^{--} structure when they are in aqueous solution at *p*H higher than 8. Infrared absorption spectra of 5′-adenylic acid in D_2O solution were obtained by Lenormant and Blout[9] at various *p*H's (or *p*D's). In the solutions at high *p*H, this compound shows a sharp band at 980 cm.$^{-1}$ and a broad band at 1100 cm.$^{-1}$. Sinsheimer, Nutter and Hopkins[10] observed strong bands at 975 and 1105 cm.$^{-1}$ for all of the seven nucleotides, which they examined, in solutions at high *p*H (both in H_2O and D_2O). In the solutions of lower *p*H these two bands are absent for every nucleotide. Hence, it is quite clear that these two bands come from the PO_3^{--} group in the nucleotide. In the light of the above studies on the HPO_3^{--} anion these are undoubtedly ascribed to the PO_3 symmetric and degenerate stretching motions.

Acknowledgments.—The author wishes to express his sincere thanks to Professor G. B. B. M. Sutherland for his kind encouragement and help in the present work, and also to give thanks to Dr. R. C. Taylor and his students for their kind help in the Raman measurements, and to Dr. S. Krimm

---

(6) E. R. Blout and M. Fields, *J. Biol. Chem.*, **178**, 335 (1949).

(7) G. B. B. M. Sutherland and M. Tsuboi, to be published.

(8) J. R. Van Wazer, "Structural Chemistry, Phosphorus Compounds, Inorganic, Encyclopedia of Chemical Technology," Vol. 10, The Interscience Encyclopedia, Inc., New York, N. Y., 1953, p. 470.

(9) H. Lenormant and E. R. Blout, *Compt. rend.*, **239**, 1281 (1954).

(10) R. L. Sinsheimer, R. L. Nutter and G. R. Hopkins, *Biochim. Biophys. Acta*, **18**, 13 (1955).

for reading the manuscript of this paper. This work was supported by a grant from the U. S. Public Health Service No. C 1559 (C4).

Experimental

Potassium hypophosphite, KH_2PO_2, having a purity of more than 98%, was purchased from Oldbury Electrochemical Co. A 50% aqueous solution was prepared in distilled water and was cleaned with active charcoal, and the same solution was used both for the Raman and infrared measurements.

The Raman spectrum was obtained photographically using a Raman spectrograph[11] in the Department of Chemistry, University of Michigan, through the kindness of Dr. R. C. Taylor. The 4358 Å. Hg emission was used as the exciting light.

Depolarization measurements were made by the two exposure method using Polaroid cylinders in a manner similar to that described by Crawford and Horwitz.[12] Exposure times were monitored by an integrating photoelectric-counter and the intensities of the lines were compared by means of a Leeds and Northrup microphotometer. Since the collimating baffles were not as closely spaced as those of Crawford and Horwitz, an appreciable convergence error was present which resulted in the maximum value for the depolarization ratio being about 0.94 instead of 0.86. A correction for this was not made, but due allowance was made in interpreting the results.

In the infrared measurement of the aqueous solution of KH_2PO_2, the solution was kept between two AgCl plates.

Infrared absorption measurements in the 4000-700 cm.$^{-1}$ region for the KH_2PO_2 solution and all other samples described in this paper were made by a Perkin-Elmer 21 spectrometer with a NaCl prism, and in the 700-400 cm.$^{-1}$ region by a Perkin-Elmer 112 spectrometer with a CsBr prism.

A thin sheet of solid KH_2PO_2, in which thin pyramidal crystals were oriented with their axes practically in one direction, was prepared on an AgCl plate. For observing the dichroism of this crystal, the AgCl polarizers were put in both sample and reference beams. In order to change the direction of polarization of the incident radiation relative to the direction of orientation, the two polarizers were rotated, instead of rotating the sample.

Crystalline calcium hypophosphite, $Ca(H_2PO_2)_2$, was also purchased from Oldbury Electrochemical Co. and had a purity of not less than 98%.

The samples of potassium phosphite, K_2HPO_3, and barium phosphite, $BaHPO_3$, were prepared from phosphorous acid (with the purity of 99%, purchased from Oldbury Electrochemical Co.) by dissolving it in water and adding KOH or $Ba(OH)_2$ until the *p*H of the solution reached 8.

The samples of barium monomethyl phosphate, $BaCH_3OPO_3$, and barium dimethyl phosphate, $Ba((CH_3O)_2PO_2)_2$, were obtained from commercial samples of roughly equimolar mixtures of mono- and dimethyl phosphate supplied by Oldbury Electrochemical Co. The two phosphates were separated from each other through solubility difference of the barium salts in water.[13]

ANN ARBOR, MICHIGAN

---

[11] G. L. Vidale and R. C. Taylor, THIS JOURNAL, **78**, 294 (1956).

[12] B. L. Crawford and W. Horwitz, *J. Chem. Phys.*, **15**, 268 (1947).

[13] W. D. Kumler and J. J. Eiler, THIS JOURNAL, **65**, 2355 (1943).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Polarography of Carbonyl Compounds. III. Semi-empirical and Empirical Relationships between Structures and Half-wave Potentials

BY DALE M. COULSON,[1] WILLIAM R. CROWELL AND S. KATHLEEN TENDICK

RECEIVED OCTOBER 18, 1956

New data are reported on the polarographic reduction of several *o*-, *m*- and *p*-substituted benzaldehydes and acetophenones in 50% dioxane solutions. Two series of empirical equations are derived expressing the relation between structures and half-wave potentials. The first series, based on the LCAO-MO theory, involve linear additive structural parameters and the second series employ Hammett's sigma constants. For each substituent the structural parameter and value of σ are calculated and tabulated. Experimentally determined half-wave potentials at zero *p*H ($E^0_{1/2}$) are compared with those obtained by use of these two series of equations and those based on the free-electron gas theory.

Recently there have been several attempts to develop theoretical or semi-empirical relationships between polarographic half-wave potentials and the structures of unsaturated carbonyl compounds. Progress has been limited by the lack of suitable experimental data. With the advent of the wide spread use of mixed aqueous-organic solvent systems, such as dioxane-water and ethanol-water, data not invalidated by adsorption effects are rapidly becoming available. Fields and Blout[2,3] studied the polyene aldehydes $CH_3(CH{=}CH)_jCHO$ with values of *j* from 1 through 5 in buffered 50% dioxane solutions. Coulson and Crowell[4,5] studied several additional compounds in similar supporting electrolyte solutions. These data were summarized in the first paper of this series.[4] Pasternak[6] and Schmid and Heilbronner[7] studied several aromatic carbonyl compounds in buffered 48% ethanol solutions, showing results that were very similar to those obtained in 50% dioxane solutions.

The present paper presents data for several *o*-, *m*- and *p*-substituted benzaldehydes and acetophenones in buffered 50% dioxane solutions. As indicated in the first paper of this series,[4] the half-wave potential, $E_{1/2}$, for the one-electron reduction of each carbonyl compound in acid solutions is a function of *p*H as indicated in equation 1

$$E_{1/2} = E_{1/2}^0 - p\text{H}(B) \qquad (1)$$

where $E_{1/2}^0$ is the half-wave potential at *p*H zero and *B* is the slope of the $E_{1/2}$ *vs.* *p*H plot. The slope of the $E_{1/2}$ *vs.* *p*H plot usually has a value of approximately 0.06 volt per *p*H unit and the electrode reaction mechanism is probably

---

[1] Stanford Research Institute, Menlo Park, California.

[2] M. Fields and E. R. Blout, THIS JOURNAL, **70**, 930 (1948).

[3] M. Fields and E. R. Blout, private communication.

[4] D. M. Coulson and W. R. Crowell, THIS JOURNAL, **74**, 1290 (1952).

[5] D. M. Coulson and W. R. Crowell, *ibid.*, **74**, 1294 (1952).

[6] R. Pasternak, *Helv. Chim. Acta*, **31**, 753 (1948).

[7] R. W. Schmid and E. Heilbronner, *ibid.*, **37**, 1453 (1954).