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The Kinetics of the Chromic Acid Oxidation of Phenylphosphonous Acid

Kalyan K. SEN GUPTA

Department of Physical Chemistry, Jadavpur University, Callcuta-32, India

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The kinetics of the oxidation of phenylphosphonous acid by chromic acid has been investigated. The rate at which gross concentration of chromium(VI) disappears follows a first order law. The rate increased with the increase of hydrogen ion concentration. The activation energy of the reaction was found to be 7.4 kcal. The effect of pyridine on the reaction rate confirmed the findings of Westheimer who showed that pyridine catalyzes the oxidation of isopropyl alcohol. It is suggested that the oxidation appears to proceed through the initial formation of an intermediate compound between the active form of phenylphosphonous acid with chromic acid which finally decomposes slowly by the rate determining step. The inactive form is finally oxidized by chromium(V) by very fast step.

Chromic acid oxidizes several inorganic and organic compounds. Westheimer[1] has reviewed works on this subject. Although chromic acid oxidation of some phosphorus compounds was not studied in detail, the oxidation of phosphorous acid has been studied by Dhar.[2] In the present investigation, the kinetics of the oxidation of phenylphosphonous acid by chromic acid has been reported.

Experimental

Reagents. The materials employed were of the highest purity available. Chromic acid was prepared from 'Anala R' potassium dichromate (E. Merck), and 60% perchloric acid (E. Merck) was used without any further purification. Manganous sulfate used was of 'Anala R' grade. Pyridine (B.D.H.) was purified by redistillation. Sodium perchlorate (Riedel) of analytical grade was also used without any further purification. All other reagents were chemically pure.

Synthesis of Phenylphosphonous Acid.[3] Benzene (205 g) was treated with phosphorous trichloride (109 g) under reflux for 30 hr with stirring in the presence of anhydrous aluminium trichloride (43 g). A stream of nitrogen was passed through the reaction mixture throughout the course of the reaction and 86% H_3PO_4 (15 m*l*) was added with vigorous shaking of the mixture. The precipitate was then removed by filtration using glass wool and excess benzene was removed by distillation. Finally the compound was vacuum-distilled and purified by redistillation to give dichlorophenylphosphine (bp 130°C/18 mmHg).

Found: Cl, 39.8%. Calcd for $C_6H_5Cl_2P$: Cl, 39.6%.

Dichlorophenylphosphine (1 vol) was then added to absolute alcohol (5 vol) with stirring, subsequently diluted with water (2 vol) and boiled for about 10 min. After benzene (2 vol) was added, the excess water and benzene were removed by distillation. The solution was then concentrated and the compound after isolation was purified by recrystallization from benzene. The compound after successive recrystallizations showed 99.6% purity which was checked by cerimetric oxidation[3] method (mp 85—86°C).

Found: C, 50.8; H, 5.1%. Calcd for $C_6H_7O_2P$: C, 50.7; H, 5.0%.

Kinetic Measurements. Rate studies were carried out at constant temperature (± 0.1°C). The reactants were brought to thermostat temperature. The reaction was then started by the rapid addition of dichromate solution to phenylphosphonous acid and mixing was achieved by stirring. At definite time intervals, 10 m*l* portions of the reaction mixture were withdrawn and quickly transferred to a flask containing freshly prepared potassium iodide solution (2 g in 20 m*l* water). The liberated iodine was then estimated by standard sodium thiosulphate solution and finally gross concentration of chromium was estimated.

Effect of Light. The hydroxy acids are oxidized by chromic acid in the presence of light.[4] Experiments showed that the reactions in the dark as well as in diffuse daylight proceeded at the same rate and hence the reactions were performed in diffuse daylight.

Results

Rate. The rate at which gross concentration of chromium(VI) disappears follows a first order rate law. It is known[5] that when $[\mathrm{Cr(VI)}] \leq 4.0 \times 10^{-3}\mathrm{M}$, the concentration of $HCrO_4^-$ ions is the same as the gross concentration of chromium(VI)

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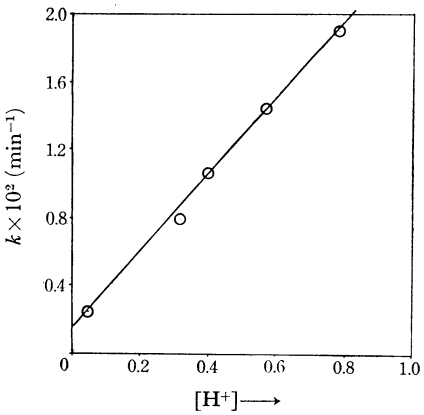
[1] F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949).

[2] N. R. Dhar, *Ann. Chim.*, **11**, 130 (1919).

[3] A. Finch, P. J. Gardner and K. K. Sen Gupta, *J. Chem. Soc.*, *B*, **1966**, 1162.

[4] A. K. Bhattacharya and N. R. Dhar, *Z. Anorg. Allg. Chem.*, **169**, 381 (1928).



$[PhPO_2H_2]=1.032\times10^{-2}$M
$[Cr(VI)]=1.666\times10^{-3}$M
Temp.=40°C; $\mu=0.607$

Fig. 1. Variation of rate with hydrogen ion concentration.

and the results indicate that $HCrO_4^-$ ions affect the rate of oxidation.

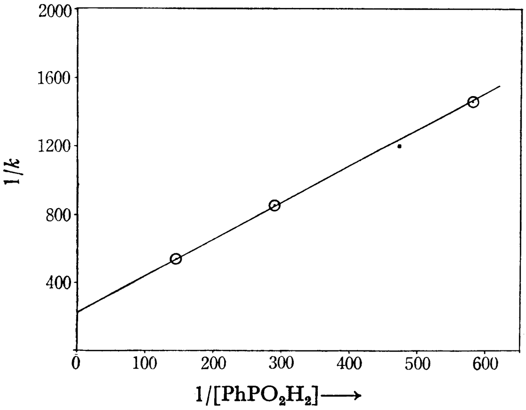
Stoichiometry. The stoichiometry was determined by allowing reaction mixtures containing a large excess of dichromate ion to stand for 48 hr at 30°C. The unreacted oxidant was then estimated by the usual procedure. The reaction may be represented by the following equation:

$$3PhPO_2H_2 + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3PhPO_3H_2 + 2Cr(III) + 4H_2O$$

(Found: 0.31 mol of oxidant per mol of the substrate)

Effect of Hydrogen Ion on the Rate. The experiments were performed at constant ionic strength and temperature. Hydrogen ion concentration was varied by the addition of perchloric acid. The ionic strength was maintained constant with sodium perchlorate. The rate increased with the increase of hydrogen ion concentration. Figure 1 represent the plot of rate constant against [H+].

Effect of Substrate Concentration on the Rate. The rates were investigated at different phenylphosphonous acid concentrations. The experiments were carried out at constant chromium(VI) concentration and temperature. The kinetic evidence indicates that an intermediate ester is formed during oxidation. The plot 1/*k* against 1/ (Substrate) labels the corresponding 1/*k* axis, indicating the formation of an intermediate compound[6] (Fig. 2). Waters and Jones[7] have shown that oxalic acid forms complexes with vanadium (V) and these complexes undergo decomposition. Since vanadium has several chemical similarities to chromium(VI), our assumption regarding the intermediate formation of an ester is quite plausible. In a more recent study, Rao and Ayyar[8] have also shown that the oxidation of oxalic acid by chromic acid proceeded through the initial formation of a metal complex. Similar is the case with glycerol[9] when it is oxidized by chromic acid. The formation of a complex species by interaction of chromium(VI) with several oxyacids has been reported by Lee and Stewart.[10]



$[Cr(VI)]=1.666\times10^{-3}$M, Temp.=40°C

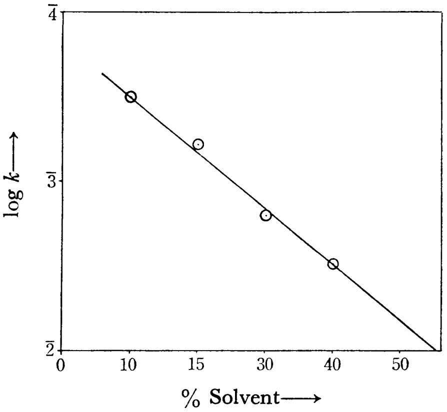
Fig. 2. Influence of substrate concentration on the rate constant.

$$HCrO_4^- + H^+ + HA \rightleftharpoons HO\text{–}CrO_2\text{–}A + H_2O$$

where,

$$A = \text{–OAc, –}SO_3H\text{, –}HCrO_4\text{, and –}OPO_3H_2$$

Influence of Solvent. The reaction was studied in various acetic acid-water binary mixtures. The



$[PhPO_2H_2]=2.038\times10^{-2}$M
$[Cr(VI)]=3.333\times10^{-3}$M
Temp=32°C

Fig. 3. Effect of solvent composition on the rate of oxidation.

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5) G. V. Bakore and S. Narain, *J. Chem. Soc.*, **1963**, 3421.

6) K. K. Sen Gupta, This Bulletin, **42**, 298 (1969).

7) W. A. Waters and J. R. Jones, *J. Chem. Soc.*, **1961**, 4757.

8) G. G. Rao and R. V. V. Ayyar, *Z. Phys. Chem.*, **236**, 17 (1967).

9) K. K. Rohatgi and P. K. Bhattacharya, *Indian J. Chem.*, **5**, 195 (1967).

10) D. G. Lee and R. Stewart, *J. Amer. Chem. Soc.*, **86**, 305 (1964).

Table 1. Variation of rate with oxidant

$[PhPO_2H_2] = 1.032\times10^{-2}$M, Temp. = 40°C, $[H^+] = 0.325$M

No.	$[Cr(VI)]\times10^{-3}$M	$k\times10^3$ (min^{-1})
1	1.666	5.527
2	3.332	3.070
3	4.998	2.303

dielectric constants of acetic acid-water mixtures are not known. Therefore, if it is assumed that the reciprocal of the dielectric constant of the mixture is proportional to the percentage of acetic acid in the solvent mixture, it has been noticed that the rate increases with the decrease in dielectric constant indicating ion dipole interaction. The increased rate of oxidation of isopropyl alcohol by chromic acid in 86.5% acetic acid has been explained[11,12] on the basis of increased protonation of $HCrO_4^-$ before the reaction in a solvent of low dielectric constant. Figure 3 shows that logarithm of the rate constant increases with the increase in the proportion of acetic acid in the mixture.

Effect of Oxidant. The reaction was also studied at different chromium(VI) concentrations, but the concentrations of phenylphosphonous acid and hydrogen ions were kept constant. Table 1 summarizes the results of the oxidation, which shows that the rate constant decreases with the increase of chromium(VI) concentration. A complication concerning chromic acid oxidation may arise due to the fact that different ionic species of chromium(VI) can exist in solution.[13] The neutral chromate ion, CrO_4^{2-}, has no oxidizing ability and in aqueous solution the dichromate ion, $Cr_2O_7^{2-}$, is formed by the rapid equilibrium

$$2HCrO_4^- \rightleftharpoons (Cr_2O_7)^{2-} + H_2O$$

Thus with the increase of the concentration of chromium(VI), a progressively smaller portion of the total amount of chromium appears in the form of an acid chromate ion, and we observe that the rate constants decrease with increasing chromium(VI) concentration.

Retarding Influence of Added Oxidizable Ions. It has been observed that commonest oxidations involve only a one-electron transfer though instances are not rare where the change involves a two-electron transfer. In the present work, the starting material is chromic acid or the acid chromate ion and the end product is trivalent chromium in a solvated condition. In the present study the rate of oxidation is diminished to one third of that in the absence of manganous ions, when the concentration of manganese(II) is 5.0×10^{-2}M. (Table 2) This is possibly due to the fact that manganous ions catalyze the disproportionation of intermediate valence states of chromium and also indicates that chromium(IV) is probably an intermediate. Since manganese dioxide does not accumulate in the reaction mixture, it may be reasonable to propose the following reaction in the presence of manganous ions.

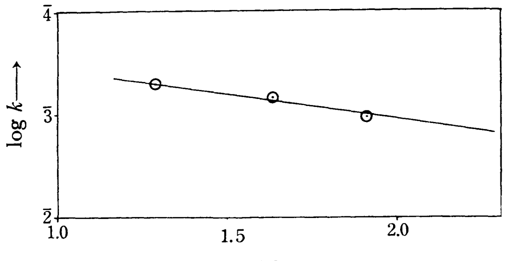
$$3Cr(IV) + Mn(II) \longrightarrow HCrO_4^- + 2Cr(III) + (Mn(II))$$

and not the reactions

$$Cr(IV) + Mn(II) \longrightarrow Cr(III) + Mn(III)$$

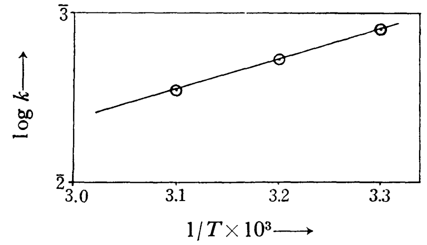
$$2Mn(III) \longrightarrow Mn(II) + MnO_2$$

as suggested by Westheimer[1] for the oxidation of arsenious acid by chromic acid.



$[PhPO_2H_2] = 1.032\times10^{-2}$M
$[Cr(VI)] = 1.666\times10^{-3}$M
$[H^+] = 0.0548$M, Temp. = 40°C

Fig. 4. Variation of ionic strength on the rate of oxidation.



$[PhPO_2H_2] = 2.036\times10^{-2}$M
$[Cr(VI)] = 1.666\times10^{-3}$M
$[H^+] = 0.01862$M
Acetic acid = 50%

Fig. 5. Arrhenius plot of log *k* *vs.* $1/T$.

Effect of Ionic Strength. The rate was studied at different ionic strengths of the reaction mixtures. The ionic strength was varied by the addition of sodium perchlorate. The rate of the reaction was increased with the increase of ionic strength. Figure 4 represents the plot of log *k* against $\mu^{1/2}$, where μ is the ionic strength.

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[11] W. A. Waters, "Mechanisms of Oxidation of Organic Compounds," Methuen's Monograph, London (1964), p. 60.

[12] M. Cohen and F. H. Westheimer, *J. Amer. Chem. Soc.*, **74**, 4387 (1952).

[13] K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York (1965), p. 71.

Table 2. Effect of Mn(II) on the rate constant
$[PhPO_2H_2] = 1.032 \times 10^{-2}$M,
$[Cr(VI)] = 1.666 \times 10^{-3}$M, $[H^+] = 0.0575$M,
Temp. = 40°C

No.	$[Mn(II)] \times 10^2$	$k \times 10^3$ (min^{-1})
1	0	0.844
2	3.3	0.4606
3	5.0	0.2763

Table 3. Effect of pyridine on the rate constant
$[PhPO_2H_2] = 1.828 \times 10^{-2}$M,
$[Cr(VI)] = 1.666 \times 10^{-3}$M, $[H^+] = 0.282$M,
$\mu = 0.25$, Temp. = 40°C.

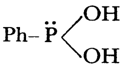
No.	[Pyridine]	$k \times 10^{-3}$ (min^{-1})	$k \times 10^{-2} / \{[H^+] - [Py]\}$
1	0	3.137	1.114
2	2×10^{-2}M	3.396	1.295
3	4×10^{-2}M	3.685	1.521
4	6×10^{-2}M	4.012	1.807

Variation of Rate with Temperature. The plot of log k against $1/T$ has been represented in Fig. 5. The experiments were carried out at constant ionic strength and hydrogen ion concentrations. From the slope of log k *vs.* $1/T$ plot, the activation energy has been calculated to be 7.4 kcal/mol. It is interesting that the activation energy calculated in the cases of the oxidation of some hydroxy acids by chromic acid are of the same orders.5) Such closeness of value suggests that same mechanism may be operative for the rate controlling step of the reaction.

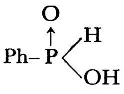
Effect of Pyridine on the Reaction Rate. The rate studies have been carried out in different pyridine concentrations. The results have been recorded in the Table 3. If pyridine catalyzes the oxidation, the value $k/\{[H^+] - [Py]\}$ is expected to increase with the increase in the concentration of pyridine which is in agreement with the experimental finding. It is also known5) that pyridine effectively removes hydrogen ions and the effective hydrogen ion concentration would correspond to $\{[H^+] - [Py]\}$. The result confirmed the findings of Westheimer who showed that pyridine catalyze the oxidation of isopropyl alcohol.

Discussion

Oxidation of a variety of organic compounds by chromic acid has been investigated. As result of the pioneering work of Westheimer and his co-workers, the details of the mechanism of some reactions have been well elucidated. In connection with the oxidation of isopropyl alcohol by chromic acid, Westheimer1) considers that the oxidation involves the rapid formation of a chromate ester, followed by the interaction with a base, and water plays the role of base in the slow rate determining step. In our case, we have also evidence for ester formation between phenylphosphonous acid and the acid chromate ion. It is well known that at very low concentration of dichromate solution5,9) ($\sim 4.0 \times 10^{-3}$M) the hexavalent chromium exists wholly as $HCrO_4^-$. This anion possibly reacts with phenylphosphonous acid to give an ester. But phenylphosphonous acid is said to exist in two forms, normal and active form which are tautomers14) of the structures:

(I) 

active

(II) 

normal

Other phosphorous compounds15) also exhibit the same sort of behaviour. Griffith and McKeown15) have postulated the interconversion between normal and active forms of phosphorous acid and also dialkyl phosphites to explain their respective results on the oxidation of phosphorous acid and dialkyl phosphites by iodine. The existence of tautomeric equilibrium of phosphorous acid has also been discussed by Finch *et al.*16) who concluded that both forms of phosphorous acid exist. Carrol and Thomas17) and recently Gupta and Mishra18) studied the oxidation of hypophosphorous acid by cerium(IV) ion and showed that the following equilibrium exists in solution.

$$H_3PO_2(\text{normal}) + H^+ \underset{k'_{H^+}}{\overset{k_{H^+}}{\rightleftarrows}} H_3PO_2(\text{active}) + H^+ \quad (1)$$

followed by the reaction of the active form with the oxidizing agent:

$$H_3PO_2 + OX \xrightarrow{k_{OX}} H_3PO_3 + \text{reaction product} \quad (2)$$

The presence of active form in the case of hypophosphorous acid has also been indicated by Jenkins and Yost19) who proved that $H\text{-}\ddot{P}\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}$ is a better electron donor than the normal form of the structure $\begin{matrix}HO\diagdown & & \diagup O\\ & P & \\ H\diagup & & \diagdown H\end{matrix}$. Therefore it is quite likely that at high acid concentration, the active form of phenylphosphonous acid is predominating although we cannot totally exclude the presence of normal form in solutions, since the monobasic

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14) A. W. Frank, *Chem. Rev.*, **61**, 389 (1961).

15) R. O. Griffith and A. McKeown, *Trans. Faraday Soc.*, **36**, 767 (1940).

16) A. Finch, P. J. Gardner and I. H. Wood, *J. Chem. Soc.*, **1965**, 746.

17) R. L. Carrol and L. B. Thomas, *J. Amer. Chem. Soc.*, **88**, 1376 (1966).

18) S. K. Mishra and Y. K. Gupta, *J. Inorg. Nucl. Chem.*, **29**, 1943 (1967).

19) W. A. Jenkins and D. M. Yost, *ibid.*, **11**, 297 (1959).

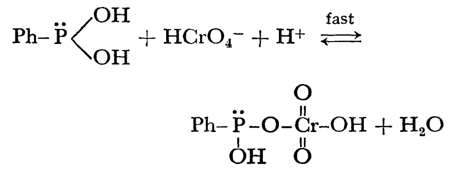
character of phenylphosphonous acid can only be explained assuming the normal form of the acid. However, the oxidation of phenylphosphonous acid may proceed in two different ways. Phenylphosphonous acid on initial oxidation may give phenol and phosphorous acid with the consumption of one oxygen atom, followed by the oxidation of the latter to H_3PO_4 with the consumption of another oxygen atom according to the equation

$$\mathrm{PhPO_2H_2 + 2O + H_2O \longrightarrow PhOH + H_3PO_4} \quad (3)$$

Some phosphonous acids also undergo scission⁹⁾ of the carbon-phosphorous bond at temperature below the disproportionation temperature. The consumption of one oxygen atom and the absence of phenol in the reaction mixture rule out the possibility of reaction (3). Consequently, phenyl phosphonous acid is oxidized to give phenyl phosphonic acid according to the equation

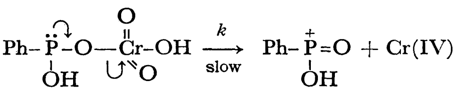
$$\mathrm{PhPO_2H_2 + O \longrightarrow PhPO_3H_2} \quad (4)$$

It is, therefore, reasonable to suppose that the oxidation of phenylphosphonous acid proceeds in the following manner. The rapid reversible formation of a chromate ester can best be explained by assuming the active form of the acid in the following way:



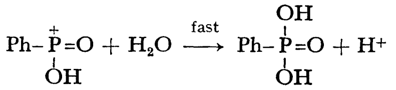
$$\mathrm{Ph{-}\ddot{P}\Big\langle^{OH}_{OH} + HCrO_4^- + H^+ \overset{fast}{\rightleftharpoons} Ph{-}\underset{OH}{\ddot{P}}{-}O{-}\overset{O}{\underset{O}{Cr}}{-}OH + H_2O} \quad (5)$$

followed by the decomposition of the ester to give a cation of the type $\mathrm{Ph{-}\overset{+}{\underset{OH}{P}}{=}O}$ and chromium(IV) by a slow rate determining step



$$\mathrm{Ph{-}\underset{OH}{\ddot{P}}{-}O{-}\overset{O}{\underset{O}{Cr}}{-}OH \xrightarrow[slow]{k} Ph{-}\overset{+}{\underset{OH}{P}}{=}O + Cr(IV)} \quad (6)$$

The cation which has been obtained in step (6) reacts with water and by fast step gives phenylphosphonic acid:



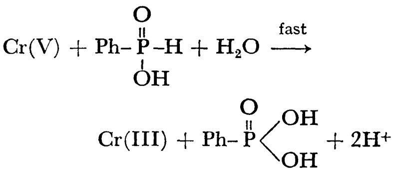
$$\mathrm{Ph{-}\overset{+}{\underset{OH}{P}}{=}O + H_2O \xrightarrow{fast} Ph{-}\overset{OH}{\underset{OH}{P}}{=}O + H^+} \quad (7)$$

Chromium(IV) produced in process (6) is then converted to chromium(V) either by reacting rapidly with chromium(VI) or chromium(IV) itself, undergoes rapid disproportionation in the following manner:

$$\mathrm{Cr(IV) + Cr(VI) \xrightarrow{fast} 2Cr(V)} \quad (8)$$

$$\mathrm{2Cr(IV) \xrightarrow{fast} Cr(III) + Cr(V)} \quad (9)$$

Similar steps have been considered in many reactions.[8,20] Finally chromium(V) formed oxidizes the inactive form of the phenylphosphonous acid rapidly abstracting two electrons, and is reduced to Cr(III) by fast step as



$$\mathrm{Cr(V) + Ph{-}\overset{O}{\underset{OH}{P}}{-}H + H_2O \xrightarrow{fast} Cr(III) + Ph{-}\overset{O}{P}\Big\langle^{OH}_{OH} + 2H^+} \quad (10)$$

The standard oxidation potential of chromium(V) - chromium(III) couple exceeds 1.75 V whereas the same for chromium(VI)-chromium(III) couple is 1.36 V. This suggests that chromium(V) is a much more active oxidant than chromium(VI) which is possibly responsible for the oxidation of inactive form of phenylphosphonous acid.

Thanks are due to Dr. M. N. Das, Head of the Physical Chemistry Section for laboratory facilities. Part of the investvation was carried out during the tenure of Scientists' Pool.

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20) K. K. Sen Gupta and S. D. Bhattacharya, *Z. Phys. Chem.* (Leipzig), **240**, 279 (1969).