(7) R. A. Bartsch, G. M. Pruss, D. M. Cook, R. L. Buswell, B. A. Bushaw, and K. E. Wiegers, *J. Am. Chem. Soc.*, **95**, 6745 (1973).

(8) S. Alunni, E. Baciocchi, R. Ruzziconi, and M. Tingoli, *J. Org. Chem.*, **39**, 3299 (1974).

(9) S. Alunni and E. Baciocchi, *J. Chem. Soc., Perkin Trans. 2*, 877 (1976).

(10) D. J. McLennan, *J. Chem. Soc., Faraday Trans. 1*, 1516 (1975).

(11) According to the Thornton model less proton transfer is expected in the transition state of the reaction with the stronger base. See E. R. Thornton, *J. Am. Chem. Soc.*, **89**, 2915 (1967), and L. J. Steffa and E. R. Thornton, *ibid.*, **89**, 6149 (1967). However, for further development of the theory, see D. A. Winey and E. R. Thornton, *ibid.*, **97**, 3102 (1975).

(12) The rate of elimination from 1-bromo-2-phenylethane increases by a factor of approximately 10^5 when the nucleophile is changed from sodium *p*-nitrophenoxide to sodium phenoxide.[1]

(13) The character of the transition state remains unchanged in the reactions of 1-bromo-2-arylethanes but becomes significantly more carbanionic in the reactions of 1-chloro-1-phenyl-2-arylethanes when the nucleophile is changed from *t*-BuOK to crown ether complexed *t*-BuOK. See S. Alunni, E. Baciocchi, and P. Perucci, *J. Org. Chem.*, **41**, 2636 (1976); **42**, 2170 (1977).

(14) W. H. Saunders, Jr., and D. H. Edison, *J. Am. Chem. Soc.*, **82**, 138 (1960).

(15) R. A. Bartsch, K. E. Wiegers, and D. M. Guritz, *J. Am. Chem. Soc.*, **96**, 430 (1974).

(16) E. Baciocchi, P. Perucci, and C. Rol, *J. Chem. Soc., Perkin Trans. 2*, 329 (1975).

Kinetics of the Baeyer–Villiger Reaction of Acetophenones with Permonophosphoric Acid[1]

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The Baeyer–Villiger reaction of acetophenones with permonophosphoric acid (H_3PO_5) has been studied kinetically in acetonitrile at 30 °C. The sole product, the corresponding aryl acetate, which is a product via aryl migration, is obtained almost quantitatively. The yields are much higher than those obtained by means of the other peroxycarboxylic acid oxidations. The rate equation is $v = k_2[\text{acetophenones}][H_3PO_5]$. The reaction is catalyzed by H_2SO_4, the rate being correlated with the acidity function (H_0). The rate-determining step is a migration step under these conditions. The apparent rate for ring-substituted acetophenones affords a Hammett ρ value of -2.55 (σ). The migration step seems to be a concerted process.

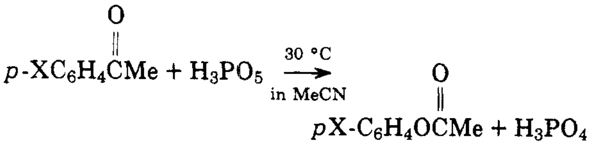
The preparation of permonophosphoric acid was discovered by Schmidlin and Massini in 1910.[2] Since then various techniques for its preparation,[3,4] decomposition mechanisms,[5] and dissociation constants[6,7] have been reported, but only a few reports have appeared on the oxidation of organic compounds, which were confined to oxidations of aromatic amines.[8] Recently, we have reported[9] on the oxidation of phenol, anisole, and toluene with permonophosphoric acid in acetonitrile; the oxidation rates for phenol and anisole (ArH) were expressed as $v = k[\text{ArH}][H_3PO_5]^2h_0$, where h_0 is Hammett's acidity function.

In the present paper, our study on the oxidations of organic compounds with H_3PO_5 was extended to the Baeyer–Villiger (B–V) reaction, in which we chose acetophenone and ring-substituted acetophenones as substrates. Ordinary B–V reactions using peroxycarboxylic acids were well studied,[10–12] where the rate equation is expressed as $v = k[\text{ketone}][\text{peracid}]$. The reaction is acid-catalyzed.[12,13] The rate-determining step may be either addition of peracid to carbonyl or migration from the adduct, depending on the substrate.[14]

This report summarizes our kinetic data on the B–V reaction of acetophenones with H_3PO_5. It was found that H_3PO_5 is a strong and excellent reagent for the B–V reaction, the rate being determined by a concerted migration which is catalyzed by strong acid.

Results and Discussion

The reaction of 0.2 molar equiv of acetophenones with H_3PO_5 was conducted in MeCN at 30 °C. The corresponding aryl acetates were obtained, and the yields were as follows: *p*-MeO, 70%; *p*-Me, 98%; H, 91%; *p*-Cl, 95%. But the corresponding methyl benzoates were not detected. Therefore, only



$$p\text{-XC}_6\text{H}_4\overset{\overset{\text{O}}{\|}}{\text{C}}\text{Me} + \text{H}_3\text{PO}_5 \xrightarrow[\text{in MeCN}]{30\ ^\circ\text{C}} p\text{X-C}_6\text{H}_4\text{O}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{Me} + \text{H}_3\text{PO}_4 \quad (1)$$

the aryl group migrates, giving aryl acetate in agreement with the migratory apptitude observed with other peracid reactions.[10] No reaction occurred with *p*-nitroacetophenone, which has a strong electron-withdrawing group.

The rates for the H_2SO_4-catalyzed B–V reaction satisfied the second-order kinetics as shown in eq 2. But in the absence

$$v = k_2[C_6H_5COMe][H_3PO_5] \qquad (2)$$

of H_2SO_4, the integral rate order was not observed because of the variation of the acidity of the system with the change of initial concentration of H_3PO_5, which is a fairly strong acid ($K_{1a} = 8 \times 10^{-2}$, $K_{2a} = 3 \times 10^{-6}$, and $K_{3a} = 2 \times 10^{-13}$ at 25 °C)[7] comparable to phosphoric acid.

A comparison of yields and rate constants with those by some other percarboxylic acids is shown in Table I. It is evident that H_3PO_5 is superior to peracetic acid and perbenzoic acid in yield and reaction rate.

Effect of Acidity. The correlation between rate constant k_2 and acidity constant H_0 of the solution was measured for the H_2SO_4-catalyzed reaction of acetophenone. A plot of log k_2 vs. $-H_0$ gave a straight line with a slope of 0.75 as shown

Table I. Comparison of the B–V Reactions of Acetophenone

Peracid	Yield, %	Rate constant
H_3PO_5[a]	91	2.9×10^{-3} M^{-1} s^{-1}
$PhCO_3H$	63[b]	1.47×10^{-5} M^{-1} s^{-1}[c]
CH_3CO_3H	33[d]	
CF_3CO_3H[e]	Quantitative	2.7×10^{-2} M^{-2} s^{-1}[f]

[a] In MeCN at 30 °C; $H_0 = -0.64$. [b] In $CHCl_3$ at 23–26 °C: S. L. Friess, *J. Am. Chem. Soc.*, **71**, 14 (1949). [c] In MeCN at 25 °C: S. L. Friess and N. Farnham, *J. Am. Chem. Soc.*, **72**, 5518 (1950). [d] In MeCN at 25 °C: W. von E. Doering and L. Speers, *J. Am. Chem. Soc.*, **72**, 5515 (1950). [e] In $ClCH_2CH_2Cl$ at 29.8 °C: M. F. Hawthorne and W. D. Emmons, *J. Am. Chem. Soc.*, **80**, 6398 (1958). [f] $v = k[CF_3CO_3H][CF_3CO_2H][R_1R_2CO]$.

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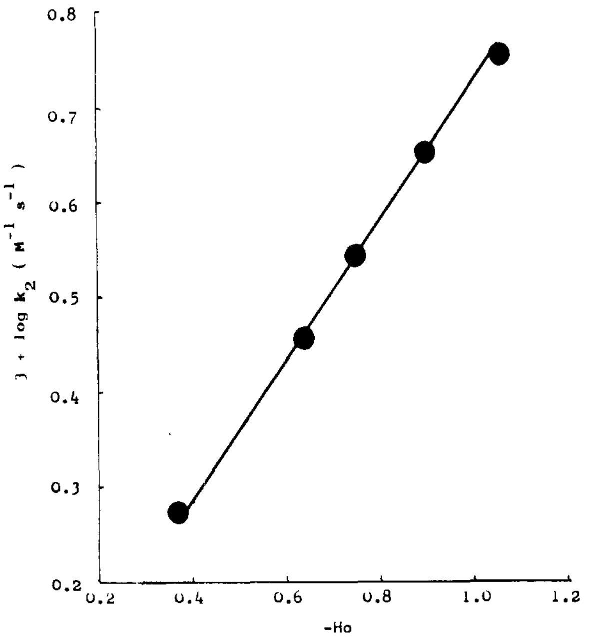
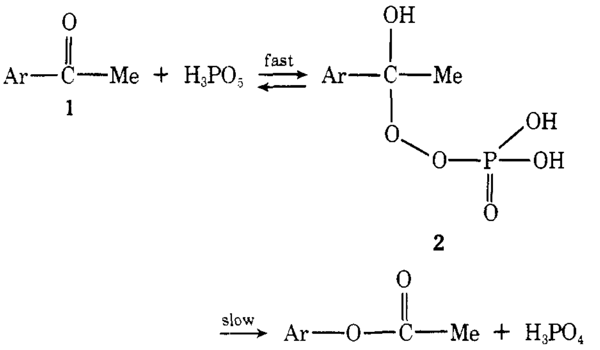


Figure 1. Effect of acidity on the second-order rate constant (k_2) in MeCN at 30 °C.

in Figure 1. This relation suggests that a proton participates in the transition state.

Substituent Effect. The effect of a ring substituent on the second-order rate constant (k_2) in rate equation $v = k_2[p\text{-X-C}_6H_4\text{COMe}][H_3PO_5]$ was studied at a constant acidity function ($H_0 = -0.64$) in MeCN at 30 °C. The rate data are listed in Table II. A Hammett plot of log k_2 vs. σ was linear with $\rho = -2.55$ and correlation coefficient = 0.991. This ρ value has the same sign as that for the trifluoroperacetic acid reactions ($\rho = -1.45$ with σ).[13] If the addition of peracid anion was rate determining, a positive ρ value would be expected, but this is not the case. Hence, the migration step seems to be rate determining.



(3)

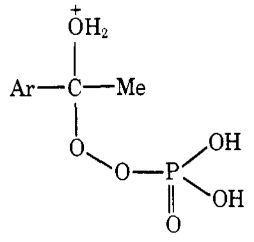
Ar = p-X-C_6H_4-

It is generally accepted[15] that a straight line plot of log k vs. $-H_0$ with a slope over 0.8 suggests unimolecular acid catalysis (A1), while a line with a slope below 0.8 suggests bimolecular acid catalysis (A2). Further, the deviation of slope from unity is often observed on account of steric and solvent effects. In our case, the linear relation of log k_2 vs. $-H_0$ with a slope of 0.75 indicates undoubtedly the participation of a proton in the transition state. Three protonated states for the adducts of permonophosphoric acid, **3–5**, are conceivable.

Table II. Second-Order Rate Constants for the Reaction of Acetophenones with H_3PO_5[a]

Substituent	Registry no.	σ	$10^3 k_2$, $M^{-1} s^{-1}$
MeO	100-06-1	−0.27	13.7
Me	122-00-9	−0.17	9.8
H	98-86-2	0	2.9
Cl	99-91-2	+0.23	0.72

[a] In MeCN at 30 °C; $H_0 = -0.64$.



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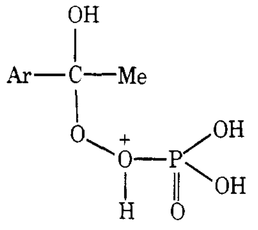

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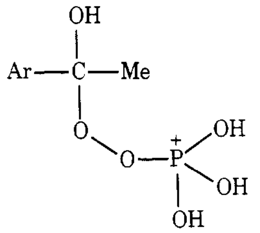

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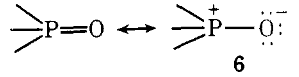
A pathway via **3** necessitates for product formation the separation of oppositely charged species (phosphoric acid anion), which should be a difficult process. A pathway via **4** or **5** does not require the separation of opposite charges, but at the same time a pathway via **4** requires the protonation at the proximity of the electron-attracting phosphorus atom, which should also pass through a fairly high energy barrier. In the last case, a pathway via **5**, the P=O bonding is a d_π–p_π bonding which is expressed as **6**, where the oxygen atom can be easily protonated. Therefore, among these three types, a pathway via **5** seems to be most appropriate.



6

The σ^+ correlation is generally observed in reactions in which the apparent positive charge is generated at the reaction center, and the charge is delocalized by aromatic resonance. In our case, the observed correlation of log k_2 vs. σ rather than σ^+ suggests that the generation of positive charge is poor on account of migration of an aryl group, which is concerted with the leaving of phosphoric acid; i.e., the migration does not occur stepwise after the complete elimination of phosphoric acid. The concerted process has been postulated by several workers, especially Hawthorne–Emmons[13] and Palmer–Fry.[16]

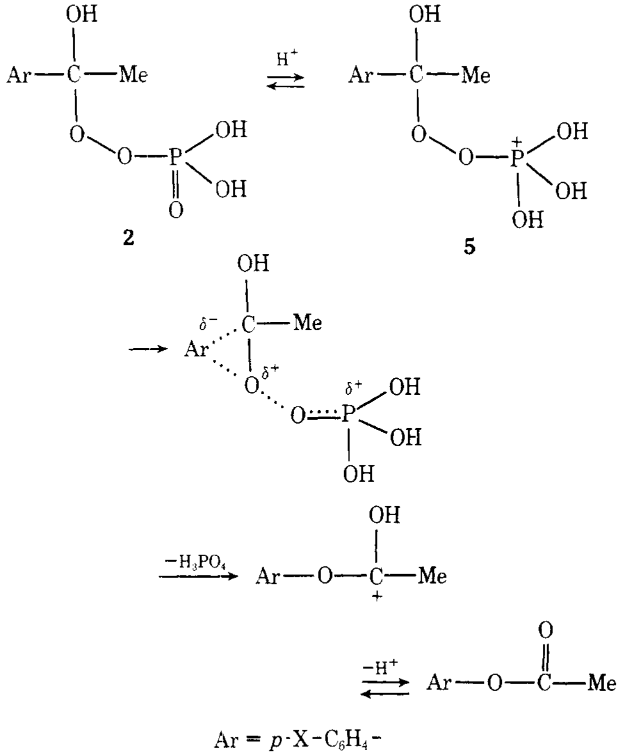
These considerations suggest the reaction mechanism as shown in Scheme I. The high reactivity of H_3PO_5 also is explained by this mechanism; i.e., the migration step is accelerated by the elimination of phosphoric acid because P–O bonding would have the strong tendency for the formation of P=O, which is very stable.[17]

Experimental Section

Materials. Acetonitrile was distilled over P_2O_5 (bp 81–82 °C). All organic reagents were protected carefully from atmospheric moisture. Acetophenone and p-nitroacetophenone were of guaranteed grade and were used without further purification. Other acetophenones were prepared by Friedel–Crafts acylation[18] and purified by fractionation. Boiling points for these ketones are as follows: p-MeO-C_6H_4COMe, 155–157 °C (26 mm); p-Me-C_6H_4COMe, 119–120 °C (30 mm); p-Cl-C_6H_4COMe, 124–125 °C (24 mm).

Preparation of Permonophosphoric Acid. To a suspension of P_2O_5 (14.2 g) in MeCN (30 mL) was added an MeCN (10 mL) solution

Scheme I



of 90% H_2O_2 (7.5 g) with stirring at −5 to −10 °C for 1 h. The mixture was stirred at room temperature for an additional 6 h. The solution contained 2-2.5 M H_3PO_5, and ca. 0.2 M H_2O_2 remained. The content of permonophosphoric acid was estimated iodometrically[19] before use, and that of H_2O_2 was estimated by $KMnO_4$ titration.[19] The oxidation with contaminated H_2O_2 was negligible because the reaction rate of a B-V reaction with H_2O_2 was smaller than 0.05 of that with H_3PO_5 (at $H_0 = -0.76$; $k_2(H_2O_2) = 1.2 \times 10^{-4}\ M^{-1}\ s^{-1}$, $k_2(H_3PO_5) = 3.5 \times 10^{-3}\ M^{-1}\ s^{-1}$).

Baeyer-Villiger Reaction. The Baeyer-Villiger reactions of acetophenones were carried out in MeCN at 30 °C. The aryl acetates produced were identified by GC-MS (a Shimadzu GCMS 7000 gas chromatograph-mass spectrometer; Silicone OV-17, 5% Shimalite W, 2.5 mm × 1.1 m). Mass spectral data were as follows: p-MeO, *m/e* 166, 124, 109, 43; p-Me, *m/e* 150, 108, 43; H, *m/e* 136, 94, 66, 43; p-Cl, *m/e* 170, 128, 43. These data agree with those of the corresponding aryl acetates.[20] No mass peaks corresponding to methyl benzoates were detected because GLC and GC-MS peaks of authentic samples of methyl benzoates did not agree with those of the products. The yields were measured by GLC (a Yanaco G 180 gas chromatograph; Silicone OV-17, 5% Shimalite W, 2.5 mm × 1.1 m). The rate was determined iodometrically by the disappearance of H_3PO_5 together with UV analysis (a Hitachi 124 spectrophotometer) of the remaining reactants.

Acidity Function.[21] All solutions were prepared before use. The indicator ratio (I) for p-nitroaniline in MeCN in the presence of H_2SO_4 was determined by means of UV spectrophotometry, and the acidity function (H_0) was calculated from the indicator ratio by eq 4 and 5. The H_0 values obtained are listed in Table III. Log K_B^{MeCN}

$$H_0 = \log K_B^{MeCN} - \log I \quad (4)$$

$$I = (\epsilon_N - \epsilon_A)/(\epsilon_A - \epsilon_S) \quad (5)$$

(indicator constant) = 0.954. ϵ_N is the molecular extinction coefficient of p-nitroaniline at the absorption peak λ_N 364 nm in neutral solution and $\epsilon_N = 16\,400$. ϵ_A is the molecular extinction coefficient of p-nitroaniline at the peak in acid solution at λ_A (nm). ϵ_S is the molecular extinction coefficient of nitrobenzene in the same solvent at λ_A (nm).

Table III. Acidity Functions (H_0) for MeCN-H_2SO_4 Derived from the Indicator Ratio of p-Nitroaniline at 30 °C

C_A,[a] N	λ_A, nm	ϵ_A	ϵ_S	I	H_0
0.026	362	794	50	21	−0.37
0.051	357	464	60	39	−0.64
0.103	350	385	75	52	−0.76
0.154	347	307	82	72	−0.90
0.206	340	250	96	105	−1.07

[a] C_A, concentration of H_2SO_4 (N); I, indicator ratio.

Registry No.—H_3PO_5, 13598-52-2; p-methoxyphenyl acetate, 1200-06-2; p-tolyl acetate, 140-39-6; phenyl acetate, 122-79-2; p-chlorophenyl acetate, 876-27-7.

References and Notes

(1) Contribution No. 245.
(2) J. Schmidlin and P. Massini, *Chem. Ber.*, **43**, 1102 (1910).
(3) G. Toennies, *J. Am. Chem. Soc.*, **59**, 555 (1937).
(4) T. Chulski, *Diss. Abstr.*, **14**, 1904 (1954).
(5) V. A. Lunenok-Burmakina, A. P. Potemskaya, and G. P. Aleeva, *Teor. Eksp. Khim.*, **2**, 549 (1966); *Chem. Abstr.*, **66**, 32309m (1967).
(6) S. H. Goh, R. B. Heslop, and J. W. Lethbridge, *J. Chem. Soc.*, 1302 (1966).
(7) C. J. Battaglia and J. O. Edwards, *Inorg. Chem.*, **4**, 552 (1965).
(8) E. Boyland and D. Manson, *J. Chem. Soc.*, 4689 (1957).
(9) Y. Ogata, I. Urasaki, K. Nagura, and N. Satomi, *Tetrahedron*, **30**, 3021 (1974).
(10) C. H. Hassall, *Org. React.*, **9**, 73 (1957).
(11) A. G. Davies, "Organic Peroxides", Butterworths, London, 1961, p 144.
(12) P. A. S. Smith, *Mol. Rearrangements 1963*, **1**, 579 (1963).
(13) M. F. Hawthorne and W. D. Emmons, *J. Am. Chem. Soc.*, **80**, 6398 (1958).
(14) Y. Ogata and Y. Sawaki, *J. Org. Chem.*, **37**, 2953 (1972).
(15) C. H. Rochester, "Acidity Functions", Academic Press, London and New York, 1970, p 195.
(16) B. W. Palmer and A. Fry, *J. Am. Chem. Soc.*, **92**, 2580 (1970).
(17) J. B. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry", 3rd ed, McGraw-Hill Kogakusha, Ltd., Tokyo, 1970, pp 789–814.
(18) R. Adams and C. R. Noller in "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1943, p 109.
(19) D. Swern, *Org. React.*, **7**, 392 (1953).
(20) E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, "Registry of Mass Spectral Data", Vol. I, Wiley, New York, N.Y., 1974.
(21) E. A. Braude, *J. Chem. Soc.*, 1971 (1948).