as described for 2-fluoroquinoline. Bathochromic shifts with protonation were pronounced for the following compounds: 2-F-Pyrm (245–256 nm), 2-F-4-MePyrm (248–260 nm), and 2-F-4,6-$(Me)_2$Pyrm (249–263 nm).

Acknowledgment. The authors thank the Murray State University Committee on Institutional Studies and Research for the generous support of this research.

Registry No. 1, 399-88-2; **2**, 407-22-7; **3**, 2369-19-9; **4**, 2369-18-8; **5**, 372-48-5; **6**, 580-21-2; **7**, 38953-33-2; **8**, 38953-32-1; **9**, 31575-35-6.

Supplementary Material Available: Enthalpies of activation (Table IV), activation parameters (Table V), a Bunnett *w* plot for **6**, **7**, and **9** (Figure 4), and a Bunnett *w** plot for **7** and **9** (Figure 5) (4 pages). Ordering information is given on any current masthead page.

Alkoxyphosphonium Salts. 3. Kinetics and Thermodynamics in Alkylation by Alkoxyphosphonium Salts[1]

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Received July 6, 1981

Several methoxyphosphonium trifluoromethanesulfonates (triflates) are characterized by the rates of methyl transfer to the 2,4-dinitrophenoxide ion. In acetone at 25 °C, the measured second-order rate constants range from about 0.2 to about 40 $M^{-1}\ s^{-1}$, putting substances of this class among the most powerful methylating agents. The methylating power is confirmed by the measurement of the equilibrium extent of methylation of the counterion, the triflate ion. The Arbuzov rearrangement of trimethyl phosphite is slow with the catalyst methyl iodide but is fast enough with the catalyst methyltrimethoxyphosphonium triflate to allow calorimetric measurement for the conversion of trimethyl phosphite to dimethyl methylphosphonate; $\Delta H = -24 \pm 2$ kcal/mol. An earlier error in the measurement of the rate of this reaction is corrected, so that the mechanism of the methyl iodide catalyzed Arbuzov reaction of trimethyl phosphite is no longer in question; the first step is rate determining.

Alkoxyphosphonium salts have long been considered intermediates in the Michaelis–Arbuzov reaction, as well as in numerous other reactions. They are, however, seldom detected, indicating that they react very rapidly with nucleophiles. The preparation of a number of these salts as the trifluoromethanesulfonates (triflates) was recently described,[2] and the rapid reaction rate of methyltrimethoxyphosphonium triflate with iodide ion was measured by an inconvenient and specialized method. A few qualitative rates of reaction of some such salts have been measured;[3,4] methyldiethylmethoxyphosphonium ion reacts only rather slowly even with iodide ion.[5] In this paper a number of rates with a standard nucleophile are measured. Equilibrium constants with the weaker nucleophile, triflate ion, are also reported.

A curiously unanswered question about a reaction as general as the Michaelis–Arbuzov reaction is the driving force of the exothermicity of this reaction. Estimates based on bond energies are quite uncertain, giving results from −15 to −44 kcal/mol.[6-8] Using methyltrimethoxyphosphonium triflate as a catalyst, we have been able to make a calorimetric measurement of ΔH in one case.

Results

Rates. Rates of reaction of several methoxyphosphonium salts with potassium 2,4-dinitrophenoxide are reported in Table I. These rates were determined in acetone solution at 25 °C by the stopped-flow method using the fall in absorbance due to the dinitrophenoxide anion for the measurement. Parallel experiments by proton NMR did not give rate constants but confirmed, in each case where rate constants are given, the formation of 2,4-dinitroanisole.

Table I. Rate Constants for $CH_3OP^+CH_3RR'$ OTF^- with Potassium 2,4-Dinitrophenoxide in Acetone at 25 °C

R	R′	*k* per methoxy group, $M^{-1}\ s^{-1}$	δ [a]
OCH_3	OCH_3	44.3	53.1
OCH_3	Ph	10.8	78.5
Ph	Ph	7.0	74.5
OCH_3	Et	0.48	99.0
Et	Et	0.2 [b]	103.5

[a] ^{31}P chemical shift, from H_3PO_4.[2] These are in reasonable agreement with some earlier reports on related compounds: Murray, M.; Schmutzler, R.; Gründemann, E.; Teichmann, H. *J. Chem. Soc. B* **1971**, 1717. Schmidpeter, A.; Brecht, H. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1969**, *24B*, 179. [b] This salt was too unstable for good measurement. The rate constant is crudely estimated (see text).

We failed to get consistent simple kinetics with any of the phosphonium salts containing an aryloxy group. This presumably relates to the impossibility of getting pure samples and contamination of these samples with methyl triflate as described below in the discussion of equilibria. When diethylmethylmethoxyphosphonium triflate was used, a yellow color developed in its acetone solution at about the same rate that the yellow color of the dinitrophenoxide disappeared after mixing. The nature of this reaction was not established, and the rate constant reported is very rough, corresponding to a rather crude correction for the unknown process.

Table I also shows the ^{31}P NMR chemical shifts, and there appears to be a correlation between the reaction rates

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Table II. Alternative Measures of Equilibrium Constants for Methyl Transfer for Tetramethoxyphosphonium Trifluoromethanesulfonate in Carbon Tetrachloride

$[(MeO)_4$-$P^+]$,[a] M	$[(MeO)_3$-PO], M	[MeO-Tf], M	K_2	K_3
0.213	1.41	3.54	23.8	109.9
0.238	1.39	4.79	27.8	117.6
0.064	1.18	1.64	30.3	476.0
0.097	1.42	1.98	29.4	333.0

[a] Analysis by NMR; free ion and ion pair not distinguished.

Table III. Equilibrium Constants for Methylation of Trifluoromethanesulfonate Ion by $AA'A''POMe^+$

A	A′	A″	solvent	K_2
OMe	OMe	Me	CCl_4	0.047 ± 0.002 [a]
OMe	OMe	OMe	CCl_4	27.8 ± 3 [a,b]
OPh	OPh	Me	$CDCl_3$	50.0 ± 5 [c]
OPh	OPh	OPh	$CDCl_3$	∞ [d]

[a] By ^1H NMR. [b] Average of values from Table II. [c] By ^{31}P NMR. [d] No salt detected.

and the chemical shifts ($\ln k = 9.1 - 0.1\delta$), presumably reflecting the increase in the rate and chemical shift with electron withdrawing substituents. The chemical shift of methylmethoxydiphenoxyphosphonium ion (δ 41.5)[2] gives a prediction of k of about 150 M^{-1} s^{-1}. This is faster than any of the measured rates but is well within the capability of the method, so this is not the reason that rates could not be measured with this compound.

Equilibria. The persistent difficulty of purifying many of the methoxyphosphonium triflates suggested that the compounds may not be stable with respect to the phosphoryl compounds and methyl triflate. This has turned out to be the case; equilibrium in the reaction (eq 1) is

$$A_3POCH_3^+,OTf^- \rightleftarrows A_3PO + CH_3OTf \qquad (1)$$

readily set up in a number of solvents. Table II shows the equilibrium constants for tetramethoxyphosphonium triflate calculated for several different concentrations by assuming little ion pair dissociation (K_2) and also by assuming complete dissociation of ion pairs, $K_3 = [A_3PO][MeOTf]/[A_3POMe^+][OTf^-]$, as measured by proton NMR, which is assumed not to distinguish the free cation and the ion pair. Not surprisingly, the assumption of the undissociated ion pair appears to be more nearly correct. Equilibrium constants K_2 are reported in Table III for several other methoxyphosphonium triflate equilibria. These equilibria are presumably quite sensitive to both solvent and salt concentration, but the trends are still reasonable. Table III shows that the trimethyl phosphate is significantly methylated by methyl triflate, but triphenyl phosphate is not.

Calorimetry. The early qualitative observation that trimethyl phosphite was rapidly isomerized by methyltrimethoxyphosphonium triflate (eq 2) led to the attempt

$$(CH_3O)_3P \xrightarrow{(CH_3O)_3PCH_3^+,^-OTf} CH_3P(O)(OCH_3)_2 \qquad (2)$$

to measure the heat evolved in the calorimeter. In chloroform solution the reaction is fast enough to follow, the NMR of parallel solutions shows that the phosphonium salt shows no net reaction, and the conversion is quantitative and fast enough. Except for limitations probably arising from the purity of the salt and the hygroscopic nature of trimethyl phosphite, the calorimetry was straightforward, giving $\Delta H = -24.2 \pm 2$ kcal/mol. We were not successful at measuring ΔH for the reaction of trimethyl phosphite with methyl triflate; the reaction (possibly because of impurities) is not quantitative. Similarly, no calorimetry was practical for the reaction of methyl triflate with dimethyl methylphosphonate. Although this is a practical preparative method for the phosphonium triflate,[2] it is not quantitative in dilute solution as shown by the nonzero equilibrium constant in Table III.

In the course of the calorimetric measurements it became clear that the rate constant for reaction 2 was far less than our previous estimate[2] of >1200 M^{-1} s^{-1} (in acetone at 0 °C). For example, in one run, from the heat evolved (uncorrected for calorimeter time constants), a 0.04 M solution of trimethyl phosphite with 0.04 M methyltrimethoxyphosphonium triflate was about half reacted in very roughly 1500 s. This corresponds to a pseudo-first-order constant of about 5×10^{-4} M^{-1} s^{-1} or an estimated second-order constant of 1.2×10^{-2} M^{-1} s^{-1}, which is probably correct within an order of magnitude.

Discussion

The rate constants reported in Table I are quite rapid for S_N2 reactions, especially since the nucleophile is a very poor one. The effects of changing the remaining groups is fairly large, but in the expected direction. The methyltrimethoxyphosphonium ion rate constant of 133 (44 per methyl group) is clearly slower than the reaction of methyl triflate with p-nitrophenoxide ion ($k = 3.1 \times 10^3$ in sulfolane at 42 °C). However, if the second nitro group were to retard the rate as much as the first (a factor of perhaps 10),[9] the estimated rate of methyl triflate with dinitrophenoxide would be 300 in a different solvent and at a higher temperature, not very different from that for the methoxyphosphonium ion.

A comparison can also be made on an equilibrium basis. The methyltrimethoxyphosphonium triflate ion pair is only somewhat more stable than the phosphonate–methyl triflate mixture, thus making it in an equilibrium sense only a slightly less powerful methylating agent than methyl triflate. Furthermore, changing the substitution pattern about the phosphonium ion can make it more powerful. The somewhat more powerful methylating power of tetramethoxyphosphonium ion than methyl triflate was also noted by Jackman[10] in sulfolane; the difference in equilibrium constants reflects both the solvent effect and the different form of the equilibrium constant, since in sulfolane, ion-pair dissociation can be more extensive.

The effects of changing the substituent on phosphorus from methyl to methoxy to phenoxy are substantial but not unexpected.

There is a discrepancy with regard to the NMR spectrum of the tetramethoxyphosphonium ion. The solution in carbon tetrachloride of trimethyl phosphite and methyl triflate had, in addition to the proton NMR peaks of these two substances, a new peak, a doublet (δ 4.1, $J_{PH} = 12$ Hz), assigned to the tetramethoxyphosphonium salt. This assignment compares to that of Jackman and co-workers[10] (δ 4.27), Cohen[11] (δ 4.30, $J_{PH} = 11.2$ Hz), and Teichmann et al.,[12] who agree with Cohen's proton NMR. The phosphorus chemical shifts reported do not agree. Cohen gives δ 51.5 downfield from phosphoric acid, whereas Teichman reports 3–5 ppm downfield from phosphoric acid.

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In our hands a new ^{31}P peak appears when methyl triflate is added to trimethyl phosphate; in chloroform-*d* this appears at δ 1.9, in rough agreement with Teichmann's value.[12] The proton-coupled spectrum showed a number of equally spaced peaks, but because of overlap with a larger amount of the trimethylphosphate multiplet, we were not able to count the weaker peaks, which would have firmly identified tetramethoxyphosphonium ion. A possible byproduct of Cohen's synthesis is the methyltrimethoxyphosphonium ion which, with δ 53.1 (Table I), could be the source of his peak (δ 51.5), but this assignment leads to different inconsistencies. The very small chemical shift for $(MeO)_4P^+$, together with the correlation with rates noted above, would make the reaction with dinitrophenoxide very fast. This has not been measured, but it certainly (by virtue of being more powerful at equilbrium than methyl triflate) can be expected to be very fast, in qualitative conformity with this prediction.

The uncertainty in the ^{31}P chemical shift might be thought to result from a dynamic effect of rapid exchange between $(MeO)_3PO$ and $(MeO)_4P^+$. No NMR peak broadening has been observed in either the proton-coupled or -decoupled phosphorus spectra or the proton spectra, nor have we ever seen[14] any methyl transfer fast enough to detect by NMR line broadening.

The results have several points of relevance to the Arbuzov reaction. The calorimetric data show that the Arbuzov conversion of trimethyl phosphite to dimethyl methylphosphonate is indeed highly exothermic. The value we present is for reaction 3 and therefore includes the heat

$$(MeO)_3P\text{ (liquid)} \xrightarrow[CHCl_3]{(MeO)_3PMe^+,{}^-OTf} (MeO)_2P(O)Me\text{ (solution)}$$

of solution of the phosphite in chloroform which we did not measure separately. The experiments used relatively large amounts of the catalyst (about 1 equiv) to make the reaction fast enough. However, the parallel NMR experiments showed that this phosphonium salt is nevertheless a true catalysis; i.e., it is not consumed, even if it is not a powerful catalyst. The result (about 24 kcal/mol) is not highly precise, for reasons we attribute to impurities as well as to the slowness of the reaction, but it appears to be the first of its nature. The phosphonium salt catalyst is in principle applicable whenever the salt can be prepared in a reasonably stable form; thus a number of other Arbuzov enthalpy changes are determinable, and we believe that a higher precision is attainable with a combination of instrumental and chemical improvements.

The rearrangements of trimethyl phosphite and of triethyl phosphite catalyzed by the appropriate intermediate phosphonium salt has been observed by Nesterov and Kessel;[13] it constitutes the chain step of the so-called autocatalytic mechanism first postulated by Rumpf.[15] It is clear that the rate of this reaction compared to that of the phosphonium salt with iodide (or the leaving group of the catalyzing alkyl ester) determines the relative importance of the classical and autocatalytic mechanisms. In our first paper we believed that the phosphite reacted even more rapidly than iodide, thus confusing the mechanistic interpretation. Now, however, with the far slower rough rate estimate by the calorimetric measurement, the confusion disappears. If the slow reaction rate is indeed correct, as suggested by the calorimetry and by the qualitative description of the preparative work, then the very fast reaction previously observed must have been misinterpreted, a possibility since the temperature-rise method is completely nonspecific. We believe that the reaction that was too fast to follow must have been just the mixing, and the temperature change was a consequence of a small heat of solution. The magnitude of the temperature change is, of course, related to the heat of the observed reaction, but when rates are the object, the heat of reaction is very poorly determined. Reaction at the rate estimated from calorimetry would have been too slow to measure by the temperature-rise method. We confirm a slow reaction rate in another solvent in work which will be published separately. Thus there is now no conflict for the mechanism of the reaction of trimethyl phosphite with methyl iodide; the first step is rate determining, and the major reaction of the intermediate phosphonium ion is with iodide ion. This mechanistic conclusion was also reached in a study of the ethyl analogue.[16] The earlier mechanistic rationalization[2] insecurely based on ion-pairing effects is now without significance.

Experimental Section

Materials. Methoxyphosphonium salts were prepared as described before.[2] Those with phenoxy groups were oily and almost certainly not very pure, in part because of the unfavorable equilibrium with methyl triflate described in the text.

Potassium 2,4-dinitrophenoxide was prepared by adding slowly 3.56 g (0.054 mol) of potassium hydroxide in a little deionized water to equivalent amounts of 2,4-dinitrophenol (Aldrich; 11.76 g in 500 mL of absolute ethanol). A fluffy yellow-orange solid precipitated; it was collected, washed with absolute ethanol, and dried over phosphorus pentoxide in a Fischer pistol at the xylene boiling point. It was stored under nitrogen.

Acetone was purified by refluxing reagent grade acetone with potassium permanganate until the purple color persisted for 30 min. It was then distilled in a nitrogen atmosphere and stored over a Linde 4A molecular sieves. Prior to use it was decanted from the molecular sieves, degassed under vacuum, and distilled by using glassware that had been rinsed with aqueous ammonia before being oven dried.

Reagent grade chloroform was passed through a column of alumina to remove ethanol, stored under nitrogen, and kept for no more than a few days before use.

Rates. Appropriate solutions were made up in acetone; the phosphonium salts were handled in nitrogen. All solutions were kept in a thermostat at 25 ± 0.05 °C immediately before use.

Rates were measured in a Durrum stopped-flow instrument by following the loss of the 2,4-dinitrophenoxide (ϵ 1.43×10^4 at 427 nm). Reactions were done under pseudo-first-order conditions with an excess of either reagent, and in most cases both ways. Absorbance was recorded on a Biomation transient recorder and was read out on a strip-chart recorder. A plot of log A or log $(A - A_\infty)$ vs. time was usually linear, and the reported rate constants are the average of at least six runs. Diethylmethylmethoxyphosphonium triflate developed a yellow color in acetone which competed with the loss of the dinitrophenoxide color. The nature of the reaction was not established, but the rate of development of absorbance at 427 was enough slower than the loss of the phenoxide color so that a rough correction for the color development could be applied, giving a rough rate constant.

No reproducible kinetics and no simple rate law applied to the color loss when any of the various phenoxyphosphonium salts were used. We attribute this to the contamination of the phosphonium salt with methyl triflate and possibly with acid. The combination suffices to explain the poor kinetic behavior.

Equilibria. The positions of equilibria were measured by integration of the proton NMR spectra, done on the Varian EM-390 instrument, or by proton-decoupled ^{31}P NMR measured unlocked under CW and with 85% H_3PO_4 concentric reference conditions, on the Varian XL-100 instrument. The measurement

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of the ^{31}P spectrum of a mixture of trimethylphosphate and methyl triflate was done on the JEOL FX90Q in the Fourier transform mode with an 85% D_3PO_4 reference and lock, and spectra were recorded both with and without proton decoupling. In none of these equilibrium studies was there any rate information, there was no change after the first spectrum was recorded, and the spectra were all as sharp as those with nonreacting systems.

Calorimetry. The calorimeter was that used by Turner and co-workers for heats of hydrogenation,[17] modified principally by closing of the hydrogen entry port and by substitution of a Kepco Model PCX-15 regulated power supply for the storage battery for calibration heating power. The methyltrimethoxyphosphonium triflate was dissolved in chloroform, and then after equilibration and an initial rating period, an ampule containing trimethyl phosphite was broken under the solution, and temperature-time recordings were taken until a final rating period was well established. Analogous reactions, but at higher concentrations, showed in the proton NMR complete conversion to dimethylmethylphosphonate and no loss of the catalyzing phosphonium salt. The calculations were conventional,[17] but the precision was not very high. We attribute the difficulty to the hygroscopic nature of trimethyl phosphite (as shown by the fact that the heat evolved seemed greater with older phosphite samples) and to the slowness of the reaction, which made the rate of heat transfer in and out of the calorimeter rather large for simple corrections in the time taken for complete reaction. Six runs yielded the average value $\Delta H = -24.2 \pm 2$ kcal/mol.

Acknowledgment. We thank the Robert A. Welch Foundation for a grant which supported this work. We thank the National Science Foundation for a Research Equipment grant providing the XL-100 NMR spectrometer and a later grant providing the JEOL FX90Q spectrometer. We thank Mr. Donald Hamp for the spectra reported on this latter instrument.

Registry No. $(CH_3O)_3P^+CH_3 \cdot OTF^-$, 64294-66-2; $(CH_3O)_2P^+(CH_3)Ph \cdot OTF^-$, 64294-67-3; $(Ph)_2P^+(CH_3)OCH_3 \cdot OTF^-$, 64294-69-5; $(CH_3O)_2P^+(CH_3)Et \cdot OTF^-$, 64294-72-0; $(Et)_2P^+(CH_3)OCH_3 \cdot OTF^-$, 64294-74-2; $(MeO)_4P^+ \cdot OTF^-$, 78870-31-2; $(PhO)_2P^+(CH_3)OCH_3 \cdot OTF^-$, 64294-70-8; $(PhO)_3P^+OCH_3 \cdot OTF^-$, 78870-33-4; potassium 2,4-dinitrophenoxide, 14314-69-3.

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Mechanism of Acid-Catalyzed Hydrolysis of Phenylketene O,O and O,S Acetals

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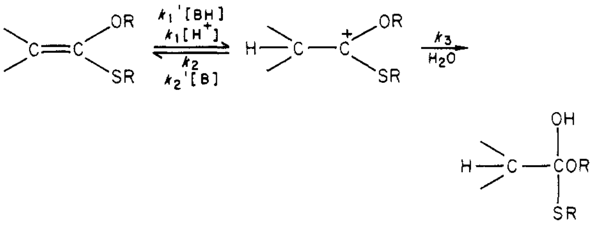
Received May 7, 1981

The hydrolyses of a phenylketene O,O acetal (1,1-dimethoxy-2-phenylethene, **1**) and an O,S acetal [(*Z*)-1-methoxy-1-(methylthio)-2-phenylethene, **2**] have been studied kinetically at 30 °C. The observed catalysis by general acids, the deuterium solvent isotope effects ($k_{H_2O}/k_{D_2O} = 5.5$ with **1**), and the lack of nucleophilic acceleration by added 2-mercaptoethanol are in accord with a mechanism involving rate-determining protonation of the double bond. The nonlinear dependence of rate on formate buffer concentration was observed in the hydrolysis of **2**, but it does not seem to be ascribable to a possible change in the rate-determining step in contrast to the previous suggestion.[5]

The acid-catalyzed hydrolysis of ketene acetals occurs through rate-determining protonation of the olefinic function followed by rapid hydration of a carbonium ion intermediate.[1-5] A similar mechanism has been established for the hydrolysis of enol ethers[6-8] and sulfides.[9,10] Ketene O,S acetals were found also to undergo hydrolysis through a similar mechanism in mineral acid solutions.[5,11] However, a possible change in rate-determining step was noted to occur in carboxylic acid buffers.[5] The nonlinear dependence of rate on buffer concentration was ascribed to a change in rate-determining step from the protonation of the doouble bond at low buffer concentrations to the hydration of a carbonium ion intermediate at higher buffer concentrations[5] (eq 1).



(1)

A similar mechanistic change in acetate buffers was suggested for the hydrolysis of an unusual cyclic enol ether, 9-methoxyoxacyclonon-2-ene.[12] Considerable efforts have been devoted, so far in vain, to explore this mechanistic change by searching for other examples of enol ether hydrolysis proceeding through rate-determining hydration.[13-18]

We have recently found that a phenylketene S,S acetal undergoes hydrolysis through preequilibrium carbon protonation even in mineral acid solutions.[19] In the present

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