

The Reactions of Isopropyl and Ethyl Iodides with Triisopropyl Phosphite in Acetonitrile

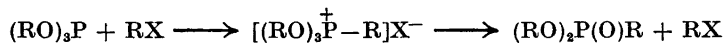
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Triisopropyl phosphite reacts very slowly with isopropyl iodide in acetonitrile, producing diisopropyl phosphite. The lack of a Michaelis-Arbuzov product is believed to be due to steric hindrance. The formation of diisopropyl phosphite is probably caused by an elimination reaction.

Ethyl iodide and triisopropyl phosphite react to give the expected Michaelis-Arbuzov product, diisopropyl ethanephosphonate. The rate is almost twice the rate of the corresponding reaction of ethyl iodide with triethyl phosphite. The rate increase is assumed to be due to a greater nucleophilicity of phosphorus in triisopropyl phosphite than in triethyl phosphite, caused by the electron donating effect of the methyl groups. The mechanism of the Michaelis-Arbuzov reaction is discussed.

Rate data on the Michaelis-Arbuzov reaction of ethyl iodide with triethyl phosphite, diethyl benzenephosphonite and ethyl benzenephosphinite in acetonitrile are previously reported to be in accordance with a two step mechanism proceeding through a phosphonium intermediate:¹



The first step was found to be rate determining, but no intermediate phosphonium compound could be detected by infrared analysis.

Quantitative studies of Michaelis-Arbuzov reactions have so far been limited to primary alkyl iodides and phosphites containing primary alkoxy groups. Several workers have reported that trialkyl phosphites containing secondary as well as tertiary alkoxy groups give satisfactory yields in the Michaelis-Arbuzov reaction with primary alkyl halogenides, whereas secondary alkyl halides either do not react or react abnormally.²⁻⁴

It therefore seemed to be of interest to investigate the latter type of reactants under the reaction conditions previously used.¹ The reactions of triisopropyl phosphite with isopropyl iodide and ethyl iodide, respectively, were selected for study.

EXPERIMENTAL

Triisopropyl phosphite was made from phosphorus trichloride and isopropyl alcohol in light petroleum (b.r. 40–60°C) using triethylamine as tertiary base. The product was freed from small amounts of diisopropyl phosphite by treatment with sodium in dry ether. Gas chromatographic analysis showed that the purity of triisopropyl phosphite was > 98 %, b.p.₁₂ 64°C, reported⁵ b.p.₁₁ 63–64°.

Diisopropyl ethanephosphonate was made by boiling triisopropyl phosphite with excess ethyl iodide. Distillation gave a pure phosphonate as shown by gas chromatographic analysis, b.p.₁₄ 98°C, n_D^{20} : 1.4130. Infrared P=O band: 1229, 1245 cm^{-1} .

Diisopropyl phosphite was obtained by boiling triisopropyl phosphite with water in acetonitrile solution, b.p.₁₀ 76°, reported⁴ b.p.₁₀ 76°. Infrared P=O band: 1262 cm^{-1} .

The identity of the products formed from the alkyl iodides and triisopropyl phosphite in acetonitrile was established by comparison of the infrared spectra of their acetonitrile solutions with the infrared spectra of the pure compounds in acetonitrile.

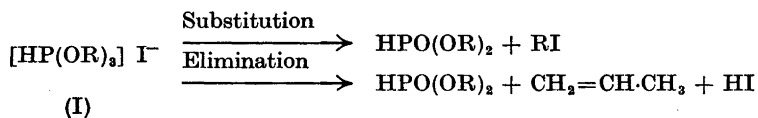
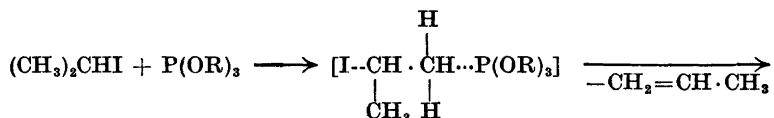
Rate measurements were performed as previously described.¹ The rate constants were calculated according to the second order equation: $dx/dt = k(a-x)(b-x)$, where x = concentration of triisopropyl phosphite at time t , and a and b are initial concentrations of triisopropyl phosphite and ethyl iodide, respectively. The second order rate constant, k , is in l/mole sec. Two solutions of the equation are needed:

$$\text{Case I: } a \neq b: F(x) = \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} = kt \quad (\text{I})$$

$$\text{Case II: } a = b: F(x) = \frac{1}{a-x} - \frac{1}{a} = kt \quad (\text{II})$$

RESULTS AND DISCUSSION

Isopropyl iodide and triisopropyl phosphite react extremely slowly in acetonitrile solution, producing diisopropyl phosphite. The fact that no alkyl substituted product could be detected by infrared analysis suggests that isopropyl iodide reacts by an elimination reaction⁴ (R = isopropyl):



The phosphonium intermediate (I) formed as a result of the elimination probably enters into a substitution to give diisopropyl phosphite and isopropyl iodide, and not into a further elimination to give propylene and hydrogen iodide instead of isopropyl iodide. Any hydrogen iodide formed would react with triisopropyl phosphite, and thus start a rapid catalytic decomposition. Another indicium against an elimination reaction of the phosphonium intermediate comes from the study of the reaction between triisopropyl phosphite and ethyl iodide. In this case, the Michaelis-Arbuzov product, diisopropyl ethanephos-

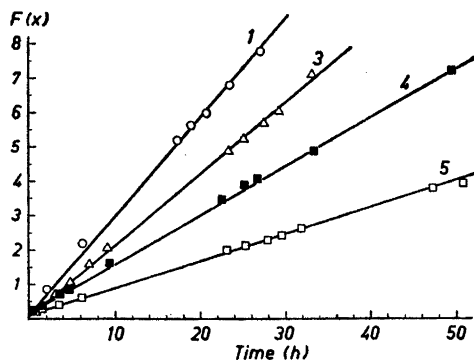


Fig. 1. Second order plots of the reaction between triisopropyl phosphite and ethyl iodide in acetonitrile with equimolecular as well as different start concentrations of reactants, plotted according to eqns. (I) and (II). The numbers on the curves refer to the series numbers in Table I.

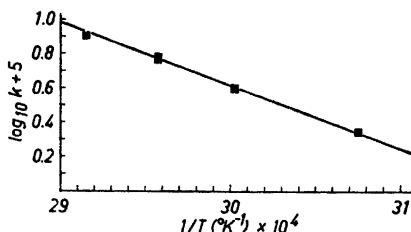
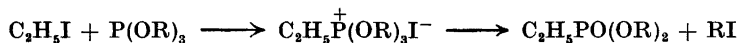


Fig. 2. The Arrhenius activation energy plot, $\log k$ against $1/T$, for the reaction between triisopropyl phosphite and ethyl iodide in acetonitrile.

phonate is the only product isolated. If the phosphonium intermediate had a tendency to decompose by an elimination reaction, propylene together with diisopropyl phosphite should also have been formed.

The absence of any substitution product in the reaction between isopropyl iodide and triisopropyl phosphite is most probably due to steric hindrance to the mutual approach of the reactants.

Since the rate of the elimination reaction between isopropyl iodide and triisopropyl phosphite is very much smaller than the rate of the Michaelis-Arbuzov reaction between ethyl iodide and triisopropyl phosphite, the latter reaction could be studied quantitatively as long as an excess of ethyl iodide over the product isopropyl iodide was present ($R = \text{isopropyl}$):



Whereas the reaction between ethyl iodide and triethyl phosphite showed pseudo first order kinetics¹ due to the regeneration of ethyl iodide, the reaction with triisopropyl phosphite obeyed second order kinetics (Fig. 1).

The calculated second order rate constants (Table 1) show that triisopropyl phosphite reacts approximately twice as fast with ethyl iodide as does triethyl phosphite. The rate increase can be attributed to the electron donating properties of the methyl groups, resulting in an increase of nucleophilicity of primary relative to secondary trialkyl phosphites. The higher nucleophilicity of phosphorus in triisopropyl phosphite as compared with triethyl phosphite is reflected in the 4–5 kcal lower activation energy of the reaction of the former compound with ethyl iodide (Table 1). The low activation energy is, however,

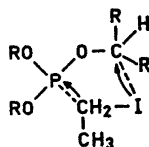
Table 1. Rate data for the reaction of primary and secondary trialkyl phosphites with ethyl iodide.

Compound	Series No.	Reaction temp.	Conc. of phosphite	Conc. of ethyl iodide	Rate const. 1/mole sec $\times 10^4$	Activation energy kcal/mole	Frequency factor log A
Triisopropyl phosphite	1	69.9	0.139	0.139	0.796	16.5	6.5
	2	65.0	0.169	0.169	0.602		
	3	65.0	0.188	0.143	0.581		
	4	60.0	0.171	0.171	0.397		
	5	52.1	0.173	0.173	0.219		
Triethyl phosphite *	—	69.9	0.1996	0.2296	0.48	21.0	9.0
	—	69.9	0.1735	0.2110	0.46		
	—	65.05	0.4409	0.4670	0.28		
	—	65.05	0.2003	0.2263	0.30		
	—	60.05	0.2039	0.2329	0.20		

* Data from a previous work.¹

almost balanced by a lower frequency factor. The latter indicates considerable steric hindrance in the formation of the transition state.

The absence of observable amounts of a phosphonium intermediate by infrared analysis in the ethyl iodide-triisopropyl phosphite reaction may indicate a S_N1 mechanism for the decomposition of the intermediate. The very low concentration of iodide ions also present (the same concentration as the phosphonium intermediate) as well as the secondary character of the alkoxy group in the phosphonium intermediate, are unfavourable to a S_N2 mechanism. But the medium, acetonitrile, makes the formation of a carbonium ion from the phosphonium intermediate less likely. A cyclic transition state as proposed previously for trialkyl phosphite-ethyl iodide¹ (see below) is unlikely from the observation of Gerrard and Green³ that trioctyl phosphite, made from (+)-octane-2-ol, reacts with ethyl iodide producing (—)-2-iodooctane.



Such a cyclic transition state would require a front side attack of the iodide ion on the alkoxy group and retention of configuration should be the result. The observed inversion is in accordance with a S_N2 mechanism, or a S_N1 mechanism where a carbonium ion of very short life time is produced.

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