

Alkylation Reactions of Triphenylphosphine and Triphenylarsine. A Kinetic Study

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The reactions of triphenylarsine and triphenylphosphine with methyl iodide and various 4-substituted benzyl halides in acetonitrile have been studied kinetically. Triphenylarsine is approximately two powers of ten less reactive than triphenylphosphine at 25 °C, the rate difference being mainly caused by the difference in activation enthalpy.

Hammett plots from the reactions with the various benzyl halides suggest that triphenylphosphine prefers to enter into a more "tight" transition state than does triphenylarsine. Triphenylarsine appears to prefer a "loose" transition state in its reactions with alkyl halides and thus resembles trialkylamines. The effect of the leaving group provides additional evidence for this suggestion.

In recent years several kinetic studies have been performed on reactions of various trivalent phosphorus compounds and alkyl halides.¹⁻⁷ With the exception of some reactions where the halogen atom undoubtedly acts as the electrophilic center,⁸ alkylation reactions of trivalent phosphorus compounds are considered typical S_N2 reactions on aliphatic carbon.³

With regard to the transition state for this class of reactions, Hudson³ has concluded, from various data, that strong bonding interaction and considerable bond breaking take place in the transition state. Thus, the transition state may be thought to be rather product-like. However, since five-membered cyclic and acyclic phosphites are known to react with alkyl halides with approximately the same rates,^{9,10} this view of a product-like transition state for alkylation reactions of trivalent phosphorus compounds is uncertain.

Alkylation reactions of trivalent arsenic species are, as well, considered as usual displacement reactions; but, since very few kinetic studies have appeared,¹¹⁻¹⁴ no conclusions can be drawn regarding the transition state of this class of reactions. Generally, trivalent arsenic compounds react with alkyl halides with rate constants which are one to two powers of ten smaller than those of the corresponding phosphorus compounds. Toward most inorganic complexes as well, trivalent arsenic compounds are considerably less reactive than are the corresponding phosphorus compounds.¹⁵ The lower reactivity of the trivalent arsenic species is assumed to be due to a number of factors: their lower basicity¹⁶⁻¹⁸ and polarizability,^{12,15} their higher ionization potential,^{19,20} and a lower energy of bond formation and a higher repulsion energy between the arsenic species and electronically saturated species.³ Due to the limited number of kinetic studies performed on alkylation reactions of trivalent arsenic compounds, it is not known whether the lower reactivity of these compounds signals a mechanistic pattern different from that of alkylation reactions of trivalent phosphorus compounds.

In the present investigation a kinetic study of various alkylation reactions of triphenylphosphine and triphenylarsine has been performed in an attempt to shed some light on these reactions, with special emphasis on the difference in reactivity of these nucleophilic species and on possible differences in the structure of the transition states. Since alkylation reactions on trialkylamines, Menshutkin reactions, appear to be the only reactions of non-

charged nucleophiles with alkyl halides which have been sufficiently examined to allow conclusions to be drawn with regard to the structure of their transition states,^{21,22} some reactions of triethylamine are included in the present study for comparison. These reactions are known to have "early" transition states.

The substrates employed were methyl iodide and various benzyl halides, the classical substrates for studies of "tight" and "loose" transition states in alkylation reactions.²⁴⁻²⁷ A dipolar aprotic solvent, acetonitrile, was used to minimize solvolytic side reactions and to allow a future comparison to be made with alkylation reactions of trivalent phosphorus and arsenic species which are unstable in protic solvents.²⁸

EXPERIMENTAL

Materials. Acetonitrile, Baker Analyzed Reagent, was purified as previously described²⁹ and flushed with nitrogen prior to use. Triphenylphosphine and triphenylarsine were purified as reported.²⁹

The various benzyl halides were either commercial products or made according to standard procedures. The solid benzyl halides were crystallized from light petroleum (40–60 °C) and from acetonitrile and washed with ice-cold acetonitrile prior to use. Benzyl bromide and benzyl chloride, both Fluka *puriss.*, were decanted from anhydrous sodium carbonate and distilled several times at reduced pressure. In this way a sample of benzyl bromide was obtained which could be crystallized at –20 °C from light petroleum. The purified benzyl halides were stored at –20 °C in darkness.

Methyl iodide, Fluka *puriss.*, was treated with silver wool and purified as reported.¹²

Separate experiments on the conductivity of the alkyl halides in acetonitrile showed these compounds to be perfectly stable, even at 50 °C, for long periods, *provided* direct sun-light was avoided. 4-Methoxy-benzyl iodide, however, was too unstable in acetonitrile even at room temperature to allow a kinetic study employing this substrate. The very unstable nature of this compound has been noted.³⁰

Rate studies. All kinetic measurements were made by conventional conductivity techniques. The reaction rates were calculated from runs performed under pseudo-first-order conditions. The concentration of the alkyl halides was in the 1.5–3 × 10⁻³ M range and was always less than 3 % of the concentration of the nucleophiles, 7.5–25 × 10⁻² M. The reactions were generally followed up to 50 to 75 % completion and the logarithmic rate plots appeared linear

throughout. For each reaction studied, the infinity reading was checked with the conductivity of the pure product of exactly the same concentration as that of the alkyl halide. Since the discrepancy was generally less than 3 %, the total error due to the uncertainty in the infinity reading was calculated to be less than 1.5 %.

The rate constants listed in the tables are averages from measurements performed in, at least, duplicate from separate weighings of reactants. From the small discrepancy observed between parallel rate determinations the listed rate constants are assumed to have an accuracy of ± 3 %.

All solutions were prepared at 25 °C, and the concentrations were corrected for the coefficient of expansion of the solvent at the various temperatures.

Conductance measurements. The measurements were performed with a Conductivity Meter CDM 3 employing an immersion type conductivity cell, CDC 304, with a cell constant of 1.07 cm. The conductivity cell was immersed with teflon fittings into two-arm mixing devices with reaction volumes from 10 to 25 ml. The conductivity of the acetonitrile was less than 1 × 10⁻⁷ Ω⁻¹ cm⁻¹.

An oil thermostat maintained all temperatures to better than ± 0.05 °C, and it was covered to minimize the effect of day-light.

Onium salts. Separate experiments showed that for all reactions studied, the onium salts were obtained in nearly quantitative yield. Since all the bromides and most of the iodides were not sufficiently soluble in acetonitrile for accurate NMR studies and since the methylene signals were significantly dependent upon the anion,^{6,31} all onium salts were transformed into their perchlorates according to a previously described procedure.²⁹ The perchlorates, after being carefully dried, were crystallized twice from acetonitrile/diethyl ether or from acetonitrile alone. The chemical shifts of the methylene protons relative to TMS together with corrected melting points of the onium perchlorates are listed in Table 1.

The NMR measurements were performed on a JEOL NMR C-60 H spectrometer, and a Spin-decoupler JNM-SO 30 counter was used to determine the resonance positions. Acetonitrile was used as the solvent.

RESULTS AND DISCUSSION

In Table 2 are listed the rate constants for the reactions between the various nucleophiles and methyl iodide in acetonitrile. Acetonitrile, an aprotic solvent and slightly more polar than methanol, is a better solvent for these quaternization reactions. The similar rate increase, ~4.3 at 25 °C, from methanol to acetonitrile

Table 1. Melting points and methylene signals in acetonitrile, relative to TMS, of substituted benzyl-triphenylphosphonium and benzyl triphenylarsonium perchlorates, $X-C_6H_4-CH_2-PPh_3^+ ClO_4^-$ and $X-C_6H_4-CH_2-AsPh_3^+ ClO_4^-$.

X	P ⁺		As ⁺		
	M.p. °C	δ	J_{H-P} (Hz)	M.p. °C δ	
4-MeO	203	4.69	14.2	155	4.81
4-Me	200	4.76	14.4	167	4.82
4-H	232	4.76	14.7	210	4.84
4-Cl	216	4.76	14.6	191	4.83
4-CN	221	4.84	15.6	221	4.90
4-NO ₂	194	4.91	15.3	202	4.95
2-NO ₂	218	5.18	14.4	132	5.24

Table 2. Rate constants for the reactions between various nucleophiles and methyl iodide in acetonitrile together with calculated activation parameters at 25.0 °C.

Temp. °C	$k_2 \times 10^3$ M ⁻¹ s ⁻¹	ΔH^* kJ mol ⁻¹	ΔS^* J K ⁻¹ mol ⁻¹
Ph ₃ P + MeI ^a			
25.0	5.94	33	-176
34.0	9.1		
44.0	14.0		
Ph ₃ As + MeI ^b			
25.0	0.0315	55	-146
34.0	0.0634		
44.0	0.128		
Et ₃ N + MeI ^c			
25.0	33.5		

$$k_2(\text{MeCN})/k_2(\text{MeOH})^{13} = {}^a 4.4, {}^b 4.2, {}^c 59.$$

for the reactions of triphenylarsine and triphenylphosphine with methyl iodide, reflects similar enthalpies of solution for the two nucleophiles.³² Triethylamine on the other hand, being well solvated in methanol due to hydrogen bonding,^{21,33} reacts considerably faster in acetonitrile than in the protic solvent.

In agreement with results from previous studies,¹¹⁻¹⁴ triphenylarsine is found to be considerably less reactive than triphenylphosphine; the latter nucleophile is 200 times more reactive than triphenylarsine toward methyl iodide at room temperature. The rate difference

appears to be caused mainly by the difference in activation enthalpies for the reactions, ~ 5 kcal mol⁻¹.^{*} The activation entropies for both reactions are very negative, but it is significantly less favourable for the triphenylphosphine-methyl iodide reaction. Although the bond angles in triphenylarsine^{34,35} and triphenylphosphine³⁶ are comparable, the large $p-\pi$ conjugation in triphenylarsine,^{37,38} mainly absent in triphenylphosphine,^{19,37} suggests an enhanced s -character for the more diffuse lone pair of the arsine. The lower rates and higher activation enthalpies for the reactions of triphenylarsine are, therefore, as expected.

In Tables 3 and 4 are collected the observed rate constants together with the calculated activation parameters for reactions with various benzyl halides. In Fig. 1 are plotted the logarithms of the rate constants *versus* the Hammett σ -values. The most important results can be summarized as follows:

1. Electron-releasing substituents in the benzyl halides can cause a greater rate enhancement for reactions with triphenylarsine than for reactions with triphenylphosphine. (Table 4 and Fig. 1).

2. Electron-withdrawing substituents reduce significantly the rates of reaction for reactions with both triphenylarsine and triethylamine, while for reactions with triphenylphosphine this effect is negligible. Actually, for reactions between benzyl bromides and triphenylphosphine, a slight rate enhancement is observed. (Table 4 and Fig. 1).

3. Although the activation enthalpies seem to increase slightly from 4-methylbenzyl iodide to 4-nitrobenzyl iodide for reactions with both triphenylarsine and triphenylphosphine, Table 3, the activation parameters do not suggest significant variations in the structure of the transition state with substituents in the benzyl iodides. It is notable, however, that triphenylphosphine reacts with the various benzyl iodides with a higher activation enthalpy, ~ 8 kJ mol⁻¹, and a more positive activation entropy, ~ 33 J K⁻¹ mol⁻¹, than for its reaction with methyl iodide, while for reactions of triphenylarsine no change is observed. (Tables 2 and 3).

When focusing first on the effect of electron-releasing substituents on reaction rates, Table

* 1 kcal = 4.184 kJ.

Table 3. Rate constants for the reactions between 4-substituted benzyl halides. X-C₆H₄-CH₂Y and triphenylphosphine, Ph₃P, and triphenylarsine, Ph₃As, in acetonitrile at various temperatures together with calculated activation parameters.

X	Y	Nuc.	Temp. °C	$k_2 \times 10^4$ M ⁻¹ s ⁻¹	ΔH^* kJ mol ⁻¹	ΔS^* J K ⁻¹ mol ⁻¹
NO ₂	Cl	Ph ₃ P	25.0	0.101	62	-134
			50.0	0.755		
NO ₂	Br	Ph ₃ P	17.0	14.6	40	-163
			25.0	23.4		
			34.0	38.3		
NO ₂	I	Ph ₃ P	17.0	98	42	-138
			25.0	163		
			34.0	276		
H	I	Ph ₃ P	18.0	121	40	-142
			25.0	182		
			34.0	308		
Me	I	Ph ₃ P	18.0	205	39	-142
			25.0	305		
			34.0	513		
NO ₂	I	Ph ₃ As	25.0	0.765	57	-134
			44.0	3.18		
			50.0	4.90		
			54.0	6.69		
H	I	Ph ₃ As	25.0	(1.37) ^a	55	-134
			34.0	2.74		
			50.0	8.31		
			56.0	12.4		
Me	I	Ph ₃ As	25.0	(2.59) ^a	55	-126
			34.0	5.08		
			50.0	15.4		
			56.0	22.8		

^a Calculated rate constants.

4 and left hand side of Fig. 1, the greater rate enhancement observed for reactions of triphenylarsine suggests that for reactions of this nucleophile with alkyl halides the formation of fractional positive charge on the carbon atom is more important than for similar reactions of triphenylphosphine. Bond breaking should therefore be more advanced in the transition state for alkylation reactions of triphenylarsine than for alkylation reactions of triphenylphosphine.²⁴⁻²⁷

The effect of the leaving group, as exemplified by the $k_2(\text{RI})/k_2(\text{RBr})$ rate ratios, Table 4, is interesting in this connection. If bond breaking in the transition state were comparable for the reactions of triphenylphosphine, triphenylarsine, and triethylamine, then one would anticipate the following sequence for the $k_2(\text{RI})/k_2(\text{RBr})$ rate ratios: Ph₃P > Ph₃As ≥ Et₃N.^{29,40} The mere fact that the rate ratios are comparable, and even slightly greater,

for the reactions of triphenylarsine than for the corresponding reactions of triphenylphosphine may be considered as additional evidence for the suggested difference in the extent of bond breaking in the transition state. In this respect it is interesting to note that reactions between triphenylarsine and alkyl chlorides are strongly catalyzed by small metal cations in aprotic solvents, while the effect is not very pronounced for reactions of triphenylphosphine.⁴¹ Presumably, triphenylarsine, because of the diffusiveness of its lone pair of electrons causing this nucleophile to be a weak base toward both the proton¹⁶⁻¹⁸ and aliphatic carbon,^{14,29,42} is only able to displace rapidly a halide ion from an alkyl halide when the carbon-halogen bond is weakened through considerable bond breaking. Electron-withdrawing substituents, destabilizing the positive charge on the benzylic carbon atom, show a distinct

Table 4. Rate constants for the reactions between triphenylarsine, triphenylphosphine and triethylamine and substituted benzyl halides, $X-C_6H_4-CH_2Y$, in acetonitrile. (Relative rates in parentheses).

X	Y=I	Y=Br	$k_2(RI)/k_2(RBr)$
Ph ₃ As; 50 °C; $k_2 \times 10^4 M^{-1} s^{-1}$			
4-CH ₃ O		9.15 (9.2)	
4-CH ₃	15.4 (1.86)	1.71 (1.74)	9.0
4-H	8.3 (1.00)	0.98 (1.00)	8.5
4-Cl	7.0 (0.84)	0.85 (0.86)	8.2
4-CN	4.9 (0.59)	0.62 (0.63)	7.9
4-NO ₂	4.9 (0.59)	0.54 (0.55)	9.0
2-NO ₂	9.4 (1.13)		
Ph ₃ P; 25.0 °C; $k_2 \times 10^3 M^{-1} s^{-1}$			
4-CH ₃ O		0.81 (3.77)	
4-CH ₃	3.05 (1.68)	0.350 (1.63)	8.7
4-H	1.82 (1.00)	0.215 (1.00)	8.5
4-Cl	1.82 (1.00)	0.238 (1.10)	8.0
4-CN	1.54 (0.85)	0.221 (1.03)	7.0
4-NO ₂	1.63 (0.90)	0.234 (1.09)	7.0
2-NO ₂	2.65 (1.46)		
Et ₃ N; 25.0 °C; $k_2 \times 10^3 M^{-1} s^{-1}$			
4-CH ₃	6.82 (1.91)		
4-H	3.57 (1.00)	0.677	5.3
4-NO ₂	1.37 (0.38)		

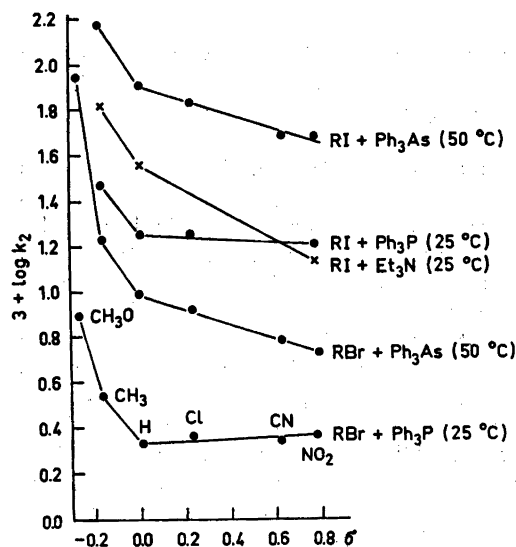


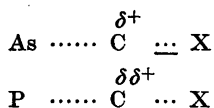
Fig. 1. The logarithms of the rate constant versus the Hammett σ constants. (R = *para*-substituted benzyl).

rate reduction for reactions of both triphenylarsine and triethylamine.

The negligible effect of electron-withdrawing substituents in benzylic halides on rates of reactions with triphenylphosphine, clearly suggests that the transition state for this class of reactions is different from that for alkylation reactions of triphenylarsine and trialkylamine. Since electron-releasing substituents show some rate enhancing effect, though less than for the corresponding reactions of triphenylarsine, some bond breaking must necessarily take place in the transition state. Presumably, the energy gain in a "tight" transition state, where some bond making takes place prior to bond rupture,^{24,43,44} by delocalization of the negative charge on the central carbon atom through neighbouring orbital overlap, outweighs the anticipated rate diminishing effect due to the electron-withdrawing substituents. A number of reactions are known,⁴³⁻⁴⁸ particularly Finkelstein reactions,⁴⁹⁻⁵¹ where 4-nitrobenzyl halides are considerably more reactive than are unsubstituted benzyl halides and U- and even J-shaped Hammett plots are observed. The reaction of triphenylphosphine, however, appears to be the first case of an uncharged nucleophile reacting with a benzyl halide where electron-withdrawing substituents have a negligible effect upon reaction rates.

It is probable that the ability of triphenylphosphine and triphenylarsine to enter into a "tight" transition state, *i.e.* a transition state with some bond making prior to bond breaking, should be related to the stability and the structure of phosphoranes and arsenanes, respectively. Recent NMR⁵² and photoelectron studies⁵³ have shown that the ylidic carbon atom in methylene-triphenylarsorane contrary to the carbon atom in methylene-triphenylphosphorane, is virtually sp^3 -hybridized, suggesting that triphenylarsine has a very limited ability to enter into a linear "tight" transition state with some π -bonding contribution. Triphenylarsine should, therefore, in its reactions with alkyl halides closely resemble uncharged nucleophiles derived from first row elements and particularly weakly basic amines. The amount of bond making prior to bond breaking in the transition state for the reactions of triphenylphosphine with alkyl halides cannot, however, be comparable with that in the transi-

tion state for the reactions between triarylphosphines and organic disulfides,^{54,55} or triarylphosphines and α -halo sulfones⁵⁶ where strictly linear Hammett plots with positive slope have been observed. The structure of the transition state for alkylation reactions of triphenylarsine and triphenylphosphine may thus be visualized as follows:



The "tighter" transition state suggested for the triphenylphosphine-alkyl halide reaction would necessarily imply that this class of reactions should be more subjected to steric hindrance than the triphenylarsine-alkyl halide reaction. As mentioned under point 3 above, the activation parameters for the reactions of triphenylphosphine with benzyl iodides are different from that of the triphenylphosphine-methyl iodide reaction while no difference is observed for the reactions of triphenylarsine. Presumably, when triphenylphosphine reacts with alkyl halides and when the steric demands of the reactants do not allow the reaction to go through a "tight" transition state (as is probably the case for triphenylphosphine reacting with benzyl halides) the phosphorus atom adjusts to a "looser" transition state of a less favourable activation enthalpy (Tables 2 and 3). The suggested difference in bond making in the transition state and thus the steric demands of reactants may therefore be the cause for the slightly greater rate enhancement from 4-nitrobenzyl iodide to 2-nitrobenzyl iodide for the reactions of triphenylarsine, ~ 1.9 , than for triphenylphosphine, ~ 1.6 , Table 4, even though the As-C (alkyl) bond length in alkyltriphenylarsonium cations is slightly longer than the P-C (alkyl) bond length in the corresponding phosphonium cations.

With regard to the non-linearity of Hammett plots for reactions of benzyl systems, Swain and Langsdorf²⁴ originally suggested that electron-withdrawing substituents might increase the positive character of the carbon atom of the C-X bond and thus render this atom more positive in the ground state than in the transition state. If this were the case,

4-nitrobenzyl halides should be expected to be relatively more reactive than unsubstituted benzyl halides toward basic nucleophiles than weakly basic ones. The data in Table 3 for reactions of trimethylamine and triphenylphosphine clearly indicate the opposite trend.

Finally, some comments with regard to the Hammond postulate⁵⁷ and the conclusion arrived at in the present study with regard to the extent of bond making in the transition state when triphenylarsine and triphenylphosphine are the nucleophilic species. This postulate may well be valuable in predicting the structure of transition states in substitution reactions when the leaving group is fixed and the nucleophile is varied provided the nucleophilic atom remains unchanged. However, when special electronic arrangements are possible due to the nucleophile, as in alkylation reactions of trivalent phosphorus compounds and, presumably, Finkelstein reactions,⁵⁸ the use of the Hammond postulate should be made with caution.⁵⁹

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