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REACTIONS AT HIGH PRESSURE, PART 18; VOLUMES OF ACTIVATION AND OF REACTION FOR THE WITTIG REACTION

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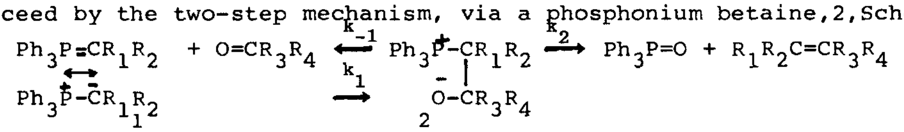
Abstract: Volumes of activation have been obtained from rate measurements between 1 and 1000 bar of reactions between triphenyl-p-nitrobenzylidenephosphorane, and a series of substituted benzaldehydes. Values of $\Delta V^{\neq}$ lie in the range -20 to -30 cm^3mol^{-1} and are somewhat solvent-dependent. The corresponding volume of reaction is less negative. These measurements are in agreement with the accepted reaction mechanism and suggest that the scope of the reaction may be extended by the use of high pressures.

The Wittig Reaction between a phosphorus ylid (phosphorane), 1, and a carbonyl compound is one of the most valuable routes to alkenes and is believed to proceed by the two-step mechanism, via a phosphonium betaine, 2, Scheme 1 [1]:



$$\underset{\underset{1}{Ph_3\overset{+}{P}-\overset{-}{C}R_1R_2}}{Ph_3P{=}CR_1R_2 \updownarrow} + O{=}CR_3R_4 \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} \underset{\underset{2}{\overset{-}{O}-CR_3R_4}}{Ph_3\overset{+}{P}-\underset{|}{C}R_1R_2} \xrightarrow{k_2} Ph_3P{=}O + R_1R_2C{=}CR_3R_4$$

Scheme 1

Relative rates of the steps involved are subject to some discussion: evidently the initial step is reversible, shown by the reaction of p-chlorobenzaldehyde with the betaine ($2, R_3{=}H, R_4{=}Ph$), preformed by a different route, to give a para-chlorophenylethene[2]. The betaine is not normally observable so it must be inferred that k_2 or $k_{-1} \gg k_1$ though, as observed by Speziale [3], further evidence is needed to distinguish between cases for which $k_{-1} \gg k_2$ and $k_{-1} \sim k_2$. In principle, the volume profile should be characteristic of the position of the transition state and might be capable of distinguishing between these cases. The initial coordination step leading to the betaine should be accompanied by a considerable reduction in volume due both to bond-formation and also to creation of dipolar charge with its concomitant solvent electrostriction, itself dependent upon the nature of the solvent [4]. One might expect the magnitude of the volume of activation for this step to be comparable with that for a dipolar (2+2)cyclo-addition for which values in the range -50 to -70 cm^3mol^{-1} have been reported[5]. On the other hand, a positive volume change should accompany the decomposition of the betaine to products due to dissociation and charge-neutralisation. If this step is rate-determining, the observed value of $\Delta V^{\neq}$ would be considerably less negative than the values quoted above. We have prepared triphenyl-p-nitrobenzal phosphorane, a stable ylide[6] and have measured rates of reaction of this compound with several substituted benzaldehydes by following the disappearance of the absorption at 505nm. Measurements were conducted varying the temperature, pressure, substituent and solvent. The Table summarises the rates of these reactions, the activation energies and volumes and the volumes of reaction.

Table

Second-Order Rate Constants for Reactions Between Triphenyl-p-nitrobenzylidene Phosphorane, $Ph_3P=CH.C_6H_4.NO_2$ and Benzaldehydes, $pX-C_6H_4CHO$.

a. Variation of Temperature; solvent: dioxan $10^2k_2/M^{-1}min^{-1}$

T/K X=	H	Cl	NO_2
296.0	0.57	4.13	80.0
303.3	1.14	11.14	140
308.5	1.96	19.9	207
313.2	2.90	32.9	286
$E_A/kJmol^{-1}$	73	93	57

b. Variation of X: T=313K, solvent dioxan

X	k_2	X	k_2
OH	0.19	Cl	2.9
OMe	0.38	CN	32.9
Me	0.78	NO_2	286
H	2.90		
ρ =	+2.7		

c. Variation of pressure, T= 298°K, k_{rel}

p/bar	X = H^a	Cl^a	H^b	H^c
1	1	1	1	1
200	3.30	3.49	3.22	
250				3.40
400	4.22	4.80	4.66	3.82
500			5.56	4.39
600	4.95	7.17	6.23	
650				5.26
800	7.17	12.4	10.6	6.68
900	14.9			7.61
1000				9.30
$\Delta V^{\neq}(\Delta V)$ cm^3mol^{-1}	-21(-19)	-29	-25(-18)	-19

(solvents: a, dioxan; b, acetonitrile; c, dichloromethane)

Discussion; the positive Hammett reaction constant, ρ =+2.7 is consistent with a nucleophilic attack on the carbonyl carbon by the ylide, but would not alone distinguish this as being rate limiting or a pre-equilibrium. The observed activation volumes, in the range -20 to -30 cm^3mol^{-1}, however, are insufficiently negative to support a mechanism in which k_1 is the slow step since this would require $k_{obs} = k_1$ and $\Delta V^{\neq}_{obs} = \Delta V^{\neq}_1$. If $k_{-1} >> k_2$ then the initial reaction is a pre-equilibrium, and the rate law becomes: $k_{obs} = K.k_2$ where $K = k_1/k_{-1}$ and $\Delta V^{\neq}_{obs} = \Delta V_e + \Delta V^{\neq}_2$ where $\Delta V_e = \Delta V^{\neq}_1 - \Delta V^{\neq}_{-1}$. ΔV_e, the pressure coefficient of the pre-equilibrium, would be very large and negative since $\Delta V^{\neq}_1$ must be negative and $\Delta V^{\neq}_{-1}$ positive for the reasons given above. $\Delta V^{\neq}_2$, however, should be considerably positive since in the decomposition of 2, charges are being neutralised and dissociation of one molecule into the two products is occurring. This would mean that $\Delta V^{\neq}_{obs}$ would be only moderately negative, not much more so than the overall volume of reaction, ΔV. The results included here support this interpretation. The activation volumes for the four Wittig reactions studied are far less negative than would be expected for a fully ionogenic associative slow step unless it lead to a very early transition state, and are only slightly more negative than ΔV. It may be concluded that values of the activation volume for the Wittig reaction fall in the range -20 to -30 cm^3 mol^{-1} which is sufficiently negative for high pressures to be of advantage in forcing difficult reactions of this type. These values correspond to a maximum rate acceleration of between 3500 and 2 x 10^5 at a pressure of 10 kbar and 25°C.

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