ACTA CHEMICA SCANDINAVICA 23 (1969) 2697–2703

Study of Reactions between Phenyl Isocyanate and Phosphine Oxides, respectively Phosphine Imines

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Rate studies of the reaction between phenyl isocyanate and five phosphine oxides are reported. The phosphine imines formed as reactive intermediates in this reaction, have been synthesized, and their reaction with phenyl isocyanate studied in separate experiments. The phosphine imines react 10^5-10^7 times more rapidly with phenyl isocyanate than the corresponding phosphine oxides.

It is shown that the five-membered cyclic phosphine oxide, 1-phenyl-1-oxa-phospholane, is 10^3 times more active as catalyst as the acyclic oxide, phenyl diethyl phosphine oxide, whereas the rate ratio between the corresponding phosphine imines in their reaction with phenyl isocyanate is only approximately 10.

Energies and entropies of activation for the reaction of phosphine oxides as well as phosphine imines with phenyl isocyanate have been calculated.

The strong catalytic effect of phospholane oxide is discussed.

Phosphine oxides have been used as catalytic agents for preparation of aryl substituted carbodiimides from aryl isocyanates. Monagle *et al.*[1] have given convincing evidences for that the catalytic effect of phosphine oxides is due to the following reactions:

$$PhN{=}C{=}O + R_3P{=}O \rightleftharpoons \underset{\displaystyle R_3P-O}{\overset{\displaystyle |\quad|}{PhN-C=O}} \rightleftharpoons R_3P{=}NPh + CO_2 \qquad (1)$$

(X_1)

$$PhN{=}C{=}O + R_3P{=}NPh \rightleftharpoons \underset{\displaystyle Ph-N-PR_3}{\overset{\displaystyle |\quad|}{PhN=C-O}} \rightleftharpoons PhN{=}C{=}NPh + R_3P{=}O \qquad (2)$$

(X_2)

Scheme I

The above reaction scheme is in agreement with 1) the observed decrease of the ^{18}O content of ^{18}O-enriched phosphine oxides and 2) the kinetics of the carbon dioxide production. The rate studies of Monagle *et al.*[1] showed that phospholene-1-oxides had outstanding catalytic activity, and it was suggested that the reason for this effect might be due to a high polarity of the P=O bond in such phosphine oxides.

Investigation of different reactions in various phospholane systems, as hydrolysis of phospholane esters,[2,4] and alkaline decomposition of corresponding phosphonium salts,[4,5] have revealed an extraordinary high rate of reaction in five-membered ring systems containing phosphorus as heteroatom as compared with acyclic or six-membered analogs. As a working hypothesis we assumed that the strong catalytic effect shown by phospholene-1-oxides in the transformation of isocyanates to carbodiimides was due to a similar effect.

The present paper reports a study of the influence of various substituents in phosphine oxides and phosphine imines upon the rate of carbodiimide production. Both steps in reaction scheme I have been investigated, the first step by measuring the carbon dioxide production through absorption in ascarite, the second step by following the formation of the infrared absorption band of diphenyl carbodiimide at 2150 cm^{-1}.

EXPERIMENTAL

Materials. Phenyl isocyanate (Fluka puriss.) was redistilled before use, and the fraction boiling at 42°C/9 mm Hg was used. The phosphine oxides were made from the respective phosphines [6–8] on treatment with hydrogen peroxide.[9,10] The oxides were freed from water by azeotropic distillation with dry benzene, after which the compounds were distilled, or recrystallized from benzene-petrolether, if they were solid: *Triphenyl phosphine oxide* m.p. 157° (lit.[9] 156°). *Ethyldiphenyl phosphine oxide* m.p. 122° (lit.[12] 122°). *Diethylphenyl phosphine oxide* m.p. 70° (lit.[13] 59–60°). *Triethyl phosphine oxide*, b.p. 116–117°/13 (lit.[14] 238–240°). *Phenyl-1-oxophospholane*, b.p. 190°/10.

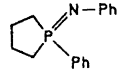
The phosphine *N*-phenylimines were synthesized according to Staudinger [15] from the respective phosphines and phenyl azide. The solid phosphine imines were recrystallized three times from ether-petrolether mixture. The liquid, triethylphosphine *N*-phenylimine, was distilled two times *in vacuo*, the last time into a receiver containing several inverted long necked weighed ampoules. At the end of distillation, the apparatus was filled with dry nitrogen at atmospheric pressure. Due to the pressure difference, the liquid imine was sucked into the ampoules which afterwards were removed and immediately sealed. *Triphenyl phosphine* N-*phenylimine*, m.p. 135° (lit.[15] 130–131°). *Ethyldiphenyl phosphine* N-*phenylimine*, m.p. 79°. Triethylphosphine *N*-phenylimine, b.p. 120°/0.35 (lit.[15] 116°/0.008). *1-phenyl-1-phospholane*-(N-*phenylimine*) m.p. 88°. Diphenyl carbodiimide was synthesized according to description in literature,[10] b.p. 170°/11, 90°/0.02 (lit.[17] 103–5°/0.1). Benzene used as solvent was distilled from $LiAlH_4$.

Kinetic measurements. 1st step. In the reaction between phenyl isocyanate and phosphine oxide, the former reactant functioned as solvent. The rate was followed by weighing the amount of carbon dioxide absorbed in ascarite as function of time. When dry nitrogen was bubbled through the reaction mixture at constant rate, very good reproducible rate values were obtained without mechanical stirring. The solid phosphine oxide was weighed and added directly to a weighed amount of phenyl isocyanate. Hygroscopic phosphine oxides, as triethyl phosphine oxide and phospholane oxide, were handled in a drying box. Measurement of CO_2-absorption was started as soon as temperature equilibrium was reached in the reaction mixture, and a steady stream of CO_2 evolved. In the experiments with the very active phospholane oxide catalyst, the phenyl isocyanate was brought

Table 1. Reaction between phenyl isocyanate and phosphine oxides.

Catalyst	Conc. of phosphine oxide	Conc. of phenyl isocyanate mole/l	Reaction temp. °C	Rate const l mole^{-1} s^{-1} $k \times 10^5$	Activation energy kcal/mole	log A l mole^{-1}s^{-1}	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ E.u.
			80.0	0.15 (calc.)				
	5.31×10^{-2}	8.65	81.2	0.16				
$Ph_3P=O$	12.70×10^{-2}	8.45	102.6	0.53	14.1	2.9	13.4	−47.6
	4.30×10^{-2}	8.30	120.0	1.14				
	3.32×10^{-2}	8.66	80.0	0.56				
$Ph_2EtP=O$	2.97×10^{-2}	8.45	102.6	2.23	16.1	4.7	15.4	−39.3
	3.03×10^{-2}	8.30	120.0	5.77				
	5.67×10^{-2}	8.83	60.0	0.37				
$PhEt_2P=O$	4.77×10^{-2}	8.66	80.0	1.97	16.6	5.6	15.9	−35.4
	7.72×10^{-2}	8.45	102.6	7.60				
	2.97×10^{-2}	9.00	40.0	0.39				
$Et_3P=O$	3.91×10^{-2}	8.83	60.0	1.40	13.6	4.1	12.9	−42.2
			80.0	4.63 (calc.)				
	2.86×10^{-2}	8.65	81.2	5.00				
	2.36×10^{-3}	9.36	0.0	15.6				
	1.96×10^{-3}	9.14	25.0	113				
	2.08×10^{-3}	9.00	40.0	280	11.6	5.5	10.9	−35.8
	1.97×10^{-3}	8.83	60.0	710				
	1.79×10^{-3}	8.65	81.2	2177				
			80.0	1995				

Table 2. Reaction between phenyl isocyanate and phosphine imines.

	Conc. of iminophosphorane 10^3 mole/l	Conc. of isocyanate 10^3 mole/l	Reaction temp. °C	Rate constant l mole^{-1}s^{-1}	Activation energy kcal/mole	log A l mole^{-1}s^{-1}	$\Delta H^{\neq}$ kcal/mole	$\Delta S^{\neq}$ E.u.
	1.225	1.091	21.5	0.66				
			25.0	0.79 (calc.)				
	1.087	1.056	25.9	0.80				
$Ph_3P=N-Ph$	1.069	1.039	33.5	1.05	9.8	7.1	9.2	−28.1
	1.225	1.091	39.5	1.37				
	1.185	1.030	40.5	1.73				
	1.173	1.017	49.3	2.73				
	1.110	1.091	23.0	2.80				
			25.0	2.93 (calc.)	9.4	7.4	8.8	−26.9
$Ph_2EtP=N-Ph$	1.110	1.091	31.6	4.13				
	1.170	1.031	39.8	6.10				
	1.157	1.019	49.1	9.95				
	1.613	1.052	23.0	11.30				
$PhEt_2P=N-Ph$			25.0	12.45 (calc.)	9.7	8.2	9.1	−23.0
	1.388	1.091	31.3	16.80				
	1.388	1.091	39.0	25.74				
	1.522	1.061	16.0	34.70				
$Et_3P=N-Ph$	1.507	1.051	23.7	50.20	9.5	8.7	8.9	−20.6
			25.0	58.20 (calc.)				
	0.305	1.091	31.5	80.7				
	1.771	1.061	16.3	69.2				
	1.756	1.052	23.0	101	9.6	9.1	9.0	−18.7
	1.756	1.052	23.3	104				
			25.0	127 (calc.)				

to the exact reaction temperature before the catalyst was added through a silionce rubber gasket with a hypodermic syringe. The accurate amount of phosphine oxide was determined by weighing the syringe before and after injection. The concentrations of phenyl isocyanate and phosphine oxide were calculated using density values of the isocyanate from the data given by Carothers,[17] extrapolated to the appropriate temperatures. The weight of carbon dioxide evolved, was plotted *versus* time as a zero order reaction.

2nd step. The reaction between phenyl isocyanate and phosphine-*N*-phenylimine was studied in benzene. The rate was followed by measuring the infrared absorption band of the product diphenyl-carbodiimide at 2150 cm^{-1}. Both reactants were studied in the concentration range around 0.001 M. A thermostated infrared cell of 6 mm path length was used. The temperature in the cell was measured with a thermocouple with an accuracy of $\pm 0.2°$. The measurements were performed on a high resolution infrared instrument, Unicam SP 100, MK2. For every rate constant calculated, 20—25 separate measurements at different concentrations, were taken. When the rate was too fast for individual measurements of the infrared absorption, the instrument was installed at fixed frequency scanning, with the recording chart moving at a constant speed. In this case, a device for mixing of the reagents in the infrared cell within 0.2 sec was constructed.

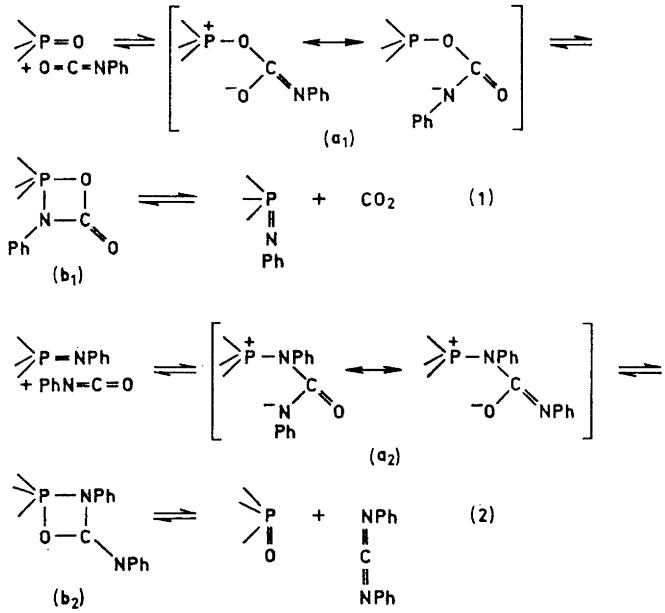
RESULTS AND DISCUSSION

In Tables 1 and 2 are summarized the rate data for the reaction between phenyl isocyanate and various phosphine oxides, respectively, phosphine imines. Energies and entropies of activation have also been calculated and recorded in the same tables.

The present rate data confirm the assumption of Monagle and coworkers [1] that the first step in scheme I is rate determining. Depending upon the substituents linked to phosphorus, the rate constant of the reaction between phosphine imine and phenyl isocyanate is 10^5—10^7 times greater than the rate constant of the corresponding reaction between phosphine oxide and phenyl isocyanate.

The activation energy of the phosphine imine-phenyl isocyanate reaction is independent of the substituents linked to phosphorus, 9.6 ± 0.2 kcal/mole. This is in remarkable contrast to the phosphine oxide-phenyl isocyanate reaction where the activation energy is found to depend strongly on the substituents. It is thus seen that the phenyl substituted phospholane oxide is characterized by a very low activation energy, 11.6 kcal/mole. This value is 5 kcal/mole lower than the value of phenyl diethyl phosphine oxide which is expected to have a comparable inductive substituent effect: both possess one phenyl group and two alkyl groups linked to phosphorus.

The very different influence of substituents on the activation energies in the two steps is difficult to understand from reaction scheme I, where two almost identical pentacovalent intermediates (X_1) and (X_2) are postulated as rate determining. These findings have led us to propose a modification of reaction scheme I in such a way that betaine intermediates have also been included in addition to the pentacovalent four-membered intermediates (reaction scheme II):



Reaction scheme II

Since oxygen is a harder nucleophile than nitrogen, oxygen is also the most reactive atom towards the hard phosphorus center in tetravalent phosphorus compounds.[18] It follows therefore that in step (1) in scheme II the rate of decomposition of the intermediate (a_1) back to reactants should be much faster than the rate of formation of the pentacovalent intermediate (b_1). This means that the latter reaction is rate determining. The rapid oxygen exchange of the P=O group observed by Monagle *et al.*[19] is in agreement with this view. In step (2), the reaction between phenyl isocyanate and phosphine imine, the same argument gives that the betaine intermediate (a_2) is more easily transformed to the pentacovalent intermediate (b_2) than back to the reactants. We may therefore assume that formation of the pentacovalent intermediate (b_1) is rate determining in step (1), whereas formation of the betaine intermediate (a_2) is rate determining in step (2). This assumption may also explain why phospholane oxide and not phospholane imine shows an exceptional high reactivity towards phenyl isocyanate, because formation of a pentacovalent intermediate is believed to be a necessary feature for the «phospholane effect» to occur. As already mentioned this seems to be the case in the hydrolysis of phospholane esters,[2,4] formation of oxyphosphoranes,[3] and in the alkaline decomposition of corresponding phosphonium salts.[4,5]

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Received February 17, 1969.