

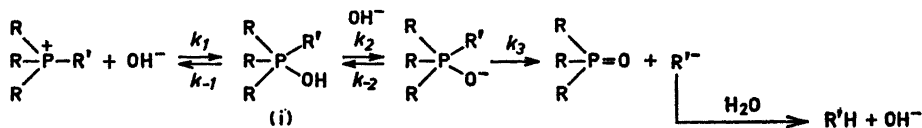
Alkaline Decomposition of *p*-Nitrobenzyl Substituted Phosponium Compounds

GUNNAR AKSNES and LEIF J. BRUDVIK

Chemical Institute, University of Bergen, Bergen, Norway

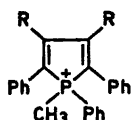
The paper reports a kinetic study of the alkaline decomposition of *p*-nitrobenzyl substituted phosphonium salts. The compounds are decomposed according to a second order rate law: first order in phosphonium ion concentration and first order in hydroxyl ion concentration. The phosphonium compound containing the phosphorus atom in a five-membered phospholan ring is decomposed approximately 1700 times as rapidly as the corresponding cyclic six-membered phosphorinan compound. Mechanisms for the decomposition are discussed.

The alkaline decomposition of phosphonium salts usually follows a third order rate law: first order in phosphonium ion concentration and second order in hydroxyl ion concentration:¹⁻⁵



Scheme A

Some times ago Aksnes and Songstad⁴ reported that the cleavage of triphenyl *p*-nitrobenzyl phosphonium bromide in alcohol-water mixture obeyed overall second order kinetics: first order in phosphonium ion concentration and first order in hydroxyl ion concentration. Correspondingly, Bergesen⁶ at this institute has observed that the alkaline cleavage of phospholium salts (1) and (2) also follows a second order rate law:



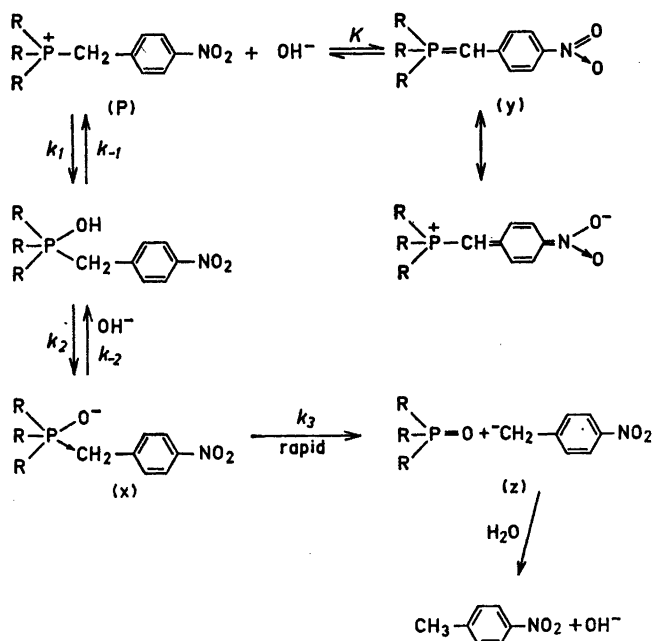
(1): R = H

(2): R = Ph

With respect to triphenyl-*p*-nitrobenzyl phosphonium bromide it was assumed⁴ that the intermediate (i) in scheme A was so unstable that the formation of this intermediate becomes rate determining (k_3 and $k_2 \gg k_{-1}$). The latter phosphonium salt was studied at constant hydroxyl ion concentration (approximately 10^{-4} M) with sufficient excess of phosphonium salt to make its concentration effectively constant throughout the measurement. Hoffmann⁷ has reported that the third order rate constant for the alkaline decomposition of various phosphonium salts appear to be somewhat dependent on the concentration of reactants. We found it therefore of interest to study the cleavage of *p*-nitrobenzyl substituted phosphonium salts under conditions where the concentration of hydroxyl ions was in great excess as compared with the concentration of phosphonium ions.

Kinetics of the alkaline decomposition of *p*-nitrobenzyl substituted phosphonium salts

In the scheme B is outlined the reaction steps for the decomposition of *p*-nitrobenzyl substituted phosphonium salts in alkaline solution. In addition to the usual reaction steps (scheme A), the formation of ylid in strongly alkaline solution plays an important role in the kinetics of these compounds:



Since the ylid (y) is highly coloured (absorption maximum at $525 \text{ m}\mu$) its rate of disappearance can be followed spectrophotometrically. If the con-

centration of phosphonium salt at any time is designated P the following equilibrium equation must be obeyed:

$$\frac{y}{(P-y)([\text{OH}]-y)} = K \quad (1)$$

where y = concentration of ylid and $[\text{OH}]$ = concentration of hydroxyl ions. When $[\text{OH}] \gg P$ which is the case in the present experiments, eqn. (1) reduces to:

$$\frac{y}{(P-y)[\text{OH}]} = K \quad (2)$$

hence,

$$y = \frac{K P [\text{OH}]}{1 + K [\text{OH}]} \quad (3)$$

$$P = \frac{y(1 + K [\text{OH}])}{K [\text{OH}]} \quad (4)$$

$$y + P = y + \frac{y(1 + K [\text{OH}])}{K [\text{OH}]} = \frac{y(1 + 2K [\text{OH}])}{K [\text{OH}]} \quad (5)$$

When $k_2 [\text{OH}]$ and $k_3 \gg k_{-1}$, the rate of phosphine oxide formation is:

$$\frac{dz}{dt} = - \frac{d(y + P)}{dt} = - \frac{1 + 2K [\text{OH}]}{K [\text{OH}]} \times \frac{dy}{dt} \quad (6)$$

But eqn. (7) for the rate of phosphine oxide formation must also be satisfied:

$$\frac{dz}{dt} = k_1 P [\text{OH}] \quad (7)$$

Eqn. (7) rearranged gives:

$$P = \frac{dz}{dt} \times \frac{1}{k_1 [\text{OH}]} \quad (8)$$

Eqn. (8) inserted in (3) gives:

$$y = \frac{K P [\text{OH}]}{1 + K [\text{OH}]} = K \frac{dz}{dt} \frac{1}{k_1 [\text{OH}]} \times \frac{[\text{OH}]}{1 + K [\text{OH}]} \quad (9)$$

Rearranging of eqn. (9) and inserting of (6) in (9) gives:

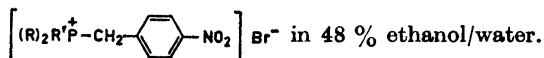
$$\frac{dz}{dt} = \frac{k_1 [\text{OH}] (1 + K [\text{OH}])}{K [\text{OH}]} y = - \frac{1 + 2K [\text{OH}]}{K [\text{OH}]} \times \frac{dy}{dt} \quad (10)$$



From eqn. (10) it follows:

$$- \frac{dy}{dt} = k_1 [\text{OH}] \times \frac{1 + K [\text{OH}]}{1 + 2K [\text{OH}]} \times y \quad (11)$$

The following conclusions can be drawn from eqn. (11):

1. As long as the hydroxyl concentration is kept constant the observed kinetics will be pseudo first order.

Table 1. Alkaline decomposition of *p*-nitrobenzyl substituted phosphonium bromide,

$(\text{R})_2\text{R}^+\text{P}-$	Temp.	NaOH mole l ⁻¹	Phosphonium bromide mole l ⁻¹	1.order, k_1 min ⁻¹	2.order, k_2 l mole ⁻¹ min ⁻¹
 (II)	18.6	0.5	2×10^{-4}	0.087	0.17
	27.0	0.5	2×10^{-4}	0.220	0.44
	34.0	0.5	2×10^{-4}	0.346	0.69
	20.0	0.5	5×10^{-4}	0.11	0.22
	20.0	1.0	5×10^{-4}	0.22	0.22
	20.0	1.5	5×10^{-4}	0.30	0.20
	20.0	2.0	5×10^{-4}	0.55	0.27
	20.0	2.5	5×10^{-4}	0.64	0.26
 (I)	26.3	0.005	2×10^{-4}	3.99	797
(n-but) ₂ P ⁺ - (III)	30.0	1.0	2×10^{-4}	1.6	1.6
	30.0	0.73	2×10^{-4}	1.1	1.5
	30.0	0.50	2×10^{-4}	6.1	1.1
	30.0	0.375	2×10^{-4}	4.8	1.3
	30.0	0.250	2×10^{-4}	3.4	1.4
(Ph) ₂ P ⁺ - (IV)	26.4	0.005	2×10^{-4}	0.955	191
	30	0.0025	2×10^{-4}	0.618	247
	30	0.005	2×10^{-4}	1.37	274
	38.2	0.0025	2×10^{-4}	1.37	548

2. When the equilibrium constant, K , for the ylid formation is small, *i.e.* $(1 + K[\text{OH}])/(1 + 2K[\text{OH}]) \approx 1$, the decomposition will also be proportional to the hydroxyl ion concentration.

RESULTS AND DISCUSSION

Typical experimental data for the disappearance of the ylid form of *p*-nitrobenzyl substituted phosphonium bromides in the presence of great excess of hydroxyl ions are shown in Fig. 1. When plotted according to the method of Guggenheim, the experimental points are seen to fit a first order rate curve. Rate data for four different *p*-nitrobenzyl substituted phosphonium bromides are collected in Table 1. Within experimental errors of the applied technique, the data confirm earlier observations that the kinetics of decomposition show first order rate dependence in phosphonium as well as in hydroxyl

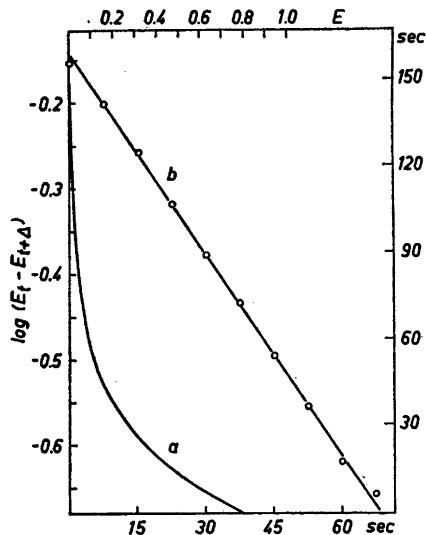


Fig. 1. Plot of experimental data for the alkaline decomposition of tributyl-*p*-nitrobenzyl phosphonium bromide, 2×10^{-4} M in 48% ethanol/water mixture at 30°C. Conc. of NaOH: 0.73 M. a) Spectrophotometer recording: dependence between optical density, E , and time. b) Guggenheim plot of a), $\log (E_t - E_{t+\Delta})$, as function of time.

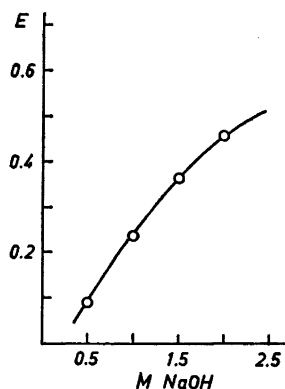
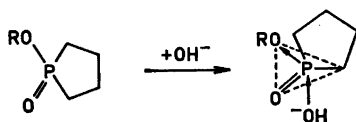


Fig. 2. Plot of optical density as function of hydroxyl concentration for 5×10^{-5} M cyclopentamethylene phenyl-*p*-nitrobenzyl bromide in 48% ethanol/water mixture. Temp. 20°C.

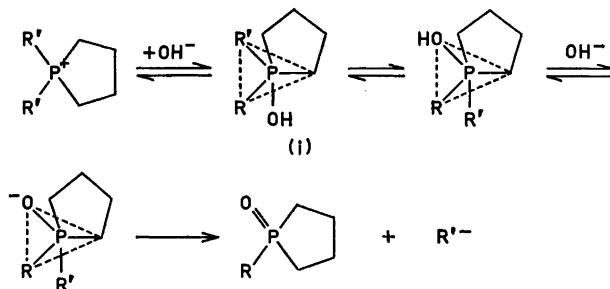
ion concentration, *i.e.* overall second order kinetics. The approximate constancy of the second order rate constant over a five-fold variation in hydroxyl concentrations, indirectly shows that the dissociation constant, K , for the ylid formation is so small that the ratio $(1 + K [\text{OH}]) / (1 + 2K [\text{OH}])$ in eqn. (11) remains approximately constant. Independent verification of this is obtained from measurements of the optical density of the ylid at the beginning of decomposition of the phosphonium salt. This is shown in Fig. 2 for cyclopentamethylene phenyl *p*-nitrobenzyl phosphonium bromide as function of hydroxyl concentration. Although the hydroxyl concentration is as high as 2.0 M, there appears to be no indication for the optical density to level out towards a maximum value. A crude estimation of the equilibrium constant from the optical density values in Fig. 2 shows K to be less than 0.1.

McEwen and co-workers¹ have postulated that the decomposition of the anion of the pentacovalent intermediate (k_2 in scheme A and B) is rate determining. With regard to alkaline decomposition of *p*-nitrobenzyl substituted phosphonium salts (scheme B), this assumption is untenable since second order rate dependence on hydroxyl ions should then be observed. However, the observed first order rate dependence on hydroxyl ion concentration is equally well satisfied by a single S_N2 displacement step from the phosphonium cation to phosphine oxide as by the intermediate steps shown in rate scheme B

where k_3 and $k_2[\text{OH}] \gg k_{-1}$. Since the rate constants k_2 and k_{-2} in scheme B represent an acid-base reaction, $k_2[\text{OH}]$ will never be expected to become rate determining in the decomposition. The mechanistic steps for the alkaline decomposition of *p*-nitrobenzyl substituted phosphonium salts might therefore be fundamentally the same as for other phosphonium salts obeying third order kinetics, and the change to second order for the former reaction is therefore due to a much greater rate constant, k_3 , *i.e.* a much more unstable anion of the pentacovalent intermediate (X in scheme B). Evidence for the presence of intermediates also in *p*-nitrobenzyl substituted phosphonium salts comes from comparison of the ratio of rate constants for decomposition of five-membered and six-membered cyclic phosphonium salts (I and II in Table 1) with the ratio of rate constants of corresponding phosphonium salts where a phenyl group is the leaving group during decomposition. The rate ratio in the former case is 1700. In the latter case where third order kinetics is observed and intermediates therefore are to be expected, the ratio is also of corresponding magnitude, approximately 1300.⁸ As argued in a previous publication,⁹ the high rate of decomposition of the five-membered phospholan compound is assumed to be due to an easy formation of a bipyramidal pentacovalent intermediate¹⁵⁻¹⁷ caused by a small C—P—C angle ($95 \pm 3^\circ$) in the phospholan ring. It was, however, shown⁹ that the rate of alkaline hydrolysis of ethyl esters of corresponding five- and six-membered phosphinic acids, which most certainly belongs to $\text{S}_{\text{N}}2\text{P}$ -reactions, are of comparable magnitude (3×10^{-5} and $12 \times 10^{-5} \text{ l M}^{-1} \text{ sec}^{-1}$ at 50°C). A geometrically favourable transition state during hydrolysis might be assumed to have the leaving ethoxy group in axial position. But this is certainly not the most energetically favourable reaction path for an $\text{S}_{\text{N}}2$ displacement since the incoming and leaving groups linked through the phosphorus atom form an angle of 90° with each other:



If, however, an intermediate (i) is formed as postulated for the alkaline decomposition of phosphonium salts, the situation is quite different since the leaving group in axial position may have time to exchange its position with the incoming apical hydroxyl group:



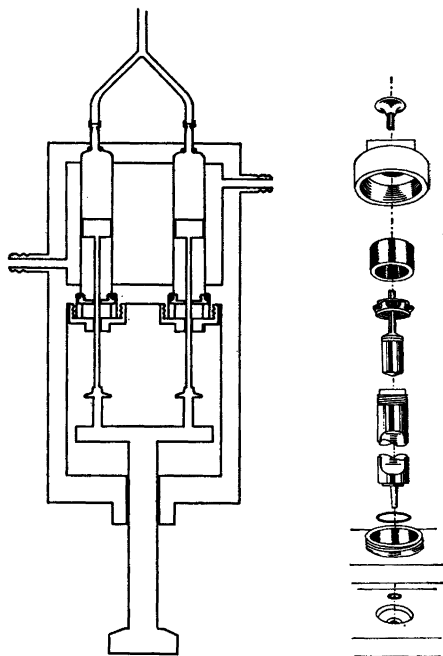


Fig. 3. Drawings of the mixing device for alkali and phosphonium bromide used in kinetic measurements.

Since the hydrolysis is divided into several steps it is possible for this reaction type to use profitably the geometrically favourable intermediate (i), and acceleration is therefore expected.

EXPERIMENTAL

Materials. *Tributyl-p-nitrobenzyl phosphonium bromide (III)* was made from tributylphosphine and *p*-nitrobenzylbromide in ether solution. The compound was recrystallized several times from an ethanol-ether mixture, m.p. 167.5–168.5°C, lit.¹⁰ 165–166°C. (Found: Br 19.10. Calc. for $C_{19}H_{33}O_2NPBr$: Br 19.12).

Triphenyl-p-nitrobenzyl phosphonium bromide (IV), was synthesized according to Kröhnke,¹¹ m.p. 263–265°C, lit. 261°C.¹¹ (decomp.), 269–270°C.¹⁰ (Found: Br 16.71. Calc. for $C_{25}H_{21}O_2NPBr$: Br 16.87).

Cyclotetramethylene phenyl-p-nitrobenzyl phosphonium bromide (I) and *cyclopentamethylene phenyl-p-nitrobenzyl phosphonium bromide (II)* were made from the respective cyclic phosphines and *p*-nitrobenzyl bromide in ether solution. The cyclic phosphines were synthesized according to descriptions by Grüttner *et al.*¹²⁻¹³ I: m.p. 150–164°C (decomp.). (Found: Br 19.3. Calc. for $C_{17}H_{19}O_2NPBr$: Br 21.0). II: m.p. 152–153°C. (Found: Br 19.6. Calc. for $C_{18}H_{21}O_2NPBr$: Br 20.3).

Kinetic measurements. The disappearance of coloured ylid (γ in scheme B) was followed in a Beckman spectrophotometer, Model DB at 525 m μ . The cells and the reaction solutions before mixing were thermostated to $\pm 0.5^\circ$. Since the half life of some of the reactions were only a few seconds a special device made of polyethylene was constructed for mixing of reactants (Fig. 3). The solution of alkali and phosphonium bromide before mixing were stored in separate compartments both of which were thermostated to the same temperature as the cells of the spectrophotometer. Through two combined pistons an equivalent amount of the reactant solutions could be effectively mixed in the sample cell in less than 0.2 sec.

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