

Phase Transfer Catalyzed Oxidation of Ketones with Borax–H₂O₂

C. S. Pande* and N. Gupta

Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla-171 005, India

Summary. Borax forms peroxy species when dissolved in 30% hydrogen peroxide which can be transferred into the organic phase when biphasic mixtures are agitated. The addition of a catalytic amount of *BTEAC* promotes the transfer. This biphasic system was used for the *Baeyer-Villiger* oxidation of several ketones insoluble in water. Effects of changing various parameters, *e.g.* temperature, time, amount of H₂O₂ etc. were investigated. At higher temperature (*ca.* 80°C), 100% conversion could be achieved in 2–4 h. The results show that under appropriate conditions this reaction is of synthetic value for the oxidation of acid-sensitive ketones using inexpensive and easily available reagents.

Keywords. *Baeyer-Villiger* oxidation; Phase transfer catalysis; Borax–H₂O₂ system.

Oxidation von Ketonen mit Borax–H₂O₂ unter Phasentransferkatalyse

Zusammenfassung. In Wasserstoffperoxid (30%) gelöstes Borax bildet Peroxyverbindungen, die durch Schütteln in die organische Phase zweiphasiger Systeme übergeführt werden können. Der Transferprozeß wird durch die Zugabe von katalytischen Mengen *BTEAC* gefördert. Die zweiphasigen Systeme wurden zur *Baeyer-Villiger*–Oxidation einiger in Wasser unlöslicher Ketone eingesetzt und die Auswirkung der Variation verschiedener Parameter (z.B. Temperatur, Zeit, Menge an H₂O₂ etc.) untersucht. Unter dem Einfluß höherer Temperaturen (*ca.* 80°C) wurde vollständige Umsetzung innerhalb von 2–4 h erreicht. Die Ergebnisse zeigen, daß die genannte Reaktion unter geeigneten Bedingungen von synthetischem Wert zur Oxidation säureempfindlicher Ketone unter Verwendung billiger und leicht verfügbarer Reagenzien ist.

Introduction

Oxidation of acyclic ketones to esters and cyclic ketones to lactones with *Caro's* acid (peroxysulfuric acid) was discovered by *Baeyer* and *Villiger* in 1899 [1]. Later on, many organic peroxy acids, *e.g.* peroxyacetic, peroxybenzoic, trifluoroperoxyacetic, and monoperoxyphthalic acid were used in presence of catalytic quantities of sulfuric or *p*-toluenesulfonic acid [2].

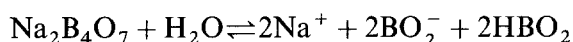
Arsonated polystyrenes and polystyrene bound phenylseleninic acid act as effective catalysts for the oxidation of ketones with H₂O₂ [3]. *Olah* and coworkers used Nafion-H, a perfluorinated resin sulfonic acid in presence of 30% H₂O₂ or *m*-chloroperoxybenzoic acid for *Baeyer-Villiger* oxidations [4]. We have used a sulfonated copolymer (styrene/divinylbenzene), a cation exchanger (AG

50W-X8, Bio-Rad), either in presence of 30% H_2O_2 or as preactivated persulfonic acid form, for such oxidations [5].

In the present work, we have investigated the use of the easily available inexpensive salt borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) in combination with H_2O_2 and *PTC* in a two-phase oxidation reaction. The net expense in the entire process was that of H_2O_2 . H_2O_2 alone is very sluggish in *Baeyer-Villiger* oxidations. Many aspects of the reaction were studied under a variety of reaction conditions.

Results and Discussion

In aqueous solution dissociation of borax occurs in the following manner:



When hydrogen peroxide is added to borax solution, the borate species are converted into their peroxy forms. We intended to investigate if these peroxy species could serve as reagents for *Baeyer-Villiger* oxidations in a biphasic system.

The transfer of these species into benzene was examined by equilibrating the water-benzene mixture in the presence of H_2O_2 , borax- H_2O_2 , and borax- H_2O_2 -*BTEAC*, treating the organic layer with $\text{KI-H}_2\text{SO}_4$ and titrating with sodium thiosulfate. A blank experiment was also run with H_2O_2 -*BTEAC* only. It was observed that, compared to the H_2O_2 system, the available amount of oxygen in the benzene layer was increased by a factor of three in borax- H_2O_2 and a factor of six in borax- H_2O_2 -*BTEAC* and H_2O_2 -*BTEAC*. This indicates a favourable transfer of the peroxy species of borate into benzene in the presence of a phase-transfer catalyst.

When borax solution is stirred with polymeric persulfonic acid for 6 h, it indicates the presence of peroxy species both by the $\text{KI-H}_2\text{SO}_4$ test and by its ability to oxidize cyclohexanone. It also appears that the reaction between borax and polymeric persulfonic acid to give peroxy species of borate is slow.

The *Baeyer-Villiger* oxidation of five different ketones under comparable conditions showed that the yields with alicyclic ketones were superior to the yields with aromatic ketones, possibly due to steric factors. It was observed (Table 3) that the yields of products from various ketones were nearly the same whether *BTEAC* had been added to the solution of borax in 30% H_2O_2 or not, although the transfer of peroxy species of boron and of H_2O_2 is much higher in the presence of *BTEAC*. In these experiments large excess of borax and of H_2O_2 was used. Table 5 proves that with other parameters remaining the same, the yield of caprolactone remains nearly unaffected on increasing the amount of H_2O_2 from 2 to 20 ml. It has been observed in preliminary experiments that H_2O_2 is transferred into the organic phase to some extent even in the absence of *BTEAC*. Under these conditions the amount of H_2O_2 and peroxy species of boron available in the organic phase may be sufficient to oxidize the ketones to the observed level.

When performing the oxidation of cyclohexanone in benzene with 30% H_2O_2 alone, the yield of the lactone was considerably lower which may be due to a very small transfer of H_2O_2 to the organic layer. Upon adding *BTEAC*, the amount of H_2O_2 transferred into the organic phase increased almost six times; however, the yield did not rise at the same degree. A combination of borax and H_2O_2 even without *PTC* is a practically suitable oxidant for *Bayer-Villiger* oxidations as is evident from

Table 3. The peroxy species of borate are, therefore, more potent oxidants for *Baeyer-Villiger* oxidations than H₂O₂ itself.

Oxidation of cyclohexanone as a representative ketone was examined as a function of time, temperature, and amount of H₂O₂ used. In all cases, the yields increased on raising any of these parameters. The rate of reaction was very fast initially but levelled out in the course of the reaction.

Chalcone, an α,β -unsaturated ketone, can react to give an epoxide, an ester or both with different oxidants. We have observed that the borax-H₂O₂ reagent affords an epoxide. In case of camphor, *Baeyer-Villiger* oxidation has been reported to give α - and β -campholides in different proportions. Under our conditions we too observed the formation of both of these products with the α -species dominating (69%).

The reactions are complete in 2–4 h when the temperature is raised to 80°C and an excess of H₂O₂ is used. The aqueous phase was only very weakly acidic (*pH* 5.1) under these conditions. This appears to be the most appropriate condition for making this reaction synthetically valuable for the oxidation of acid-sensitive ketones, using inexpensive and easily available reagents.

Experimental

The yields of the products were in all cases determined by GLC on a Hewlett-Packard Model 5840A chromatograph under the following conditions: detector mode, FID; column, UCW 982, 80–100 mesh size, 12' long; isothermal mode; carrier gas, nitrogen; flow rate, 30 ml/min; sample volume, 2–10 μ l of the organic phase; chart speed, 0.25 cm/min. Peaks were identified from the retention time of reference compounds. Peak area ratios represented the percentage of the compounds in the mixture studied. The injection temperature, FID temperature, and column temperature for reaction mixtures for different ketones are given in Table 1.

Transfer of peroxy species from aqueous to organic phase

The peroxy species transfer was studied under four different conditions (Table 2). Each flask was shaken vigorously for 20 minutes and left to stand overnight. Organic phases were shaken with 10% KI (5 ml) and 2*N* H₂SO₄ (5 ml), and the iodine liberated in the organic phase was titrated against *N*/200 sodium thiosulfate solution.

Table 1. Conditions for GLC analysis of ketones

Compound	Injection temperature (°C)	FID temperature (°C)	Column temperature (°C)
Cyclohexanone	200	250	150
Cyclopentanone	200	250	130
Camphor	200	250	100
Acetophenone	200	250	210
Benzophenone	250	250	150
Chalcone	200	250	100

Baeyer-Villiger oxidation of ketones

The ketone (1 mmol) was dissolved in 20 ml of benzene, and a solution of borax (4 mmol, 1.5 g) dissolved in 20 ml of 30% H₂O₂ was added. The two-phase mixture was stirred at 55°C for 6 h, and the yields of the products were determined. The reactions were repeated with the addition of benzyltriethylammonium chloride (*BTEAC*, 100 mg), and the yields were determined after 6 and 24 h.

The ketones oxidized by this procedure were cyclohexanone, cyclopentanone, camphor, acetophenone, benzophenone, and chalcone. Table 3 shows the results.

Table 2. Transfer of peroxy species into benzene

	Flask 1	Flask 2	Flask 3	Flask 4
	H ₂ O ₂ (1 ml)	H ₂ O ₂ (1 ml)	H ₂ O ₂ (1 ml)	H ₂ O ₂ (1 ml)
	Benzene (10 ml)	Benzene (10 ml)	Benzene (10 ml)	Benzene (10 ml)
	H ₂ O (1 ml)	Borax (200 mg)	Borax (200 mg)	<i>BTEAC</i> (50 mg)
		H ₂ O (1 ml)	<i>BTEAC</i> (50 mg)	H ₂ O (1 ml)
			H ₂ O (1 ml)	
Volume of sodium thiosulfate solution consumed	1 ml	3 ml	6 ml	6 ml

Table 3. Yields of products

Compound	Without <i>BTEAC</i> , 6 h (%)	With <i>BTEAC</i> , 6 h (%)	With <i>BTEAC</i> 24 h (%)
Cyclohexanone	79	82	100
Cyclopentanone	71	72	98
Camphor	69 ¹ , 20 ²	69.7 ¹ , 21.6 ²	72.2 ¹ , 23 ²
Acetophenone	40.1	42	61.4
Benzophenone	30.6	33	54
Chalcone	41 ³	42 ³	63 ³

¹Compared with α -campholide prepared by the known method [6]; ²compared with β -campholide prepared by the known method [7]; ³epoxide, as compared with the epoxide prepared by known method [8]

Table 4. Effect of reaction time on the yield of caprolactone

Time	Yield (%)	Time	Yield (%)	Time	Yield (%)
5 min	0.00	60 min	69.5	6 h	82
10 min	25.3	90 min	70.0	12 h	84
15 min	68.7	2 h	71	18 h	95.6
30 min	69.2	4 h	77	24 h	100

Dependence of the yield of caprolactone on reaction time

Cyclohexanone (0.2 ml, 1 mmol) in benzene (20 ml), borax (4 mmol, 1.5 g) in 30% H₂O₂ (20 ml), and BTEAC (100 mg) were stirred at 55 °C. Samples were withdrawn at different intervals of time and analyzed by GLC. Table 4 shows the results.

Effect of amount of H₂O₂ on the yield of caprolactone

Oxidation of cyclohexanone (0.2 ml) in 20 ml of benzene was carried out at 55 °C for 6 h in presence of BTEAC (100 mg), borax (1.5 g), and varying amounts of 30% H₂O₂. Yields of caprolactone as determined by GLC are presented in Table 5.

Effect of both elevated temperature and increased amount of H₂O₂ on the reaction

Oxidation of cyclohexanone (0.2 ml) was carried out at 55 °C and 80 °C, and the amount of H₂O₂ was increased in successive experiments. Progress of the reaction was monitored on TLC; after completion, the yield of the product was determined by GLC. Oxidation of other ketones was performed analogously (Table 6).

Oxidation of cyclohexanone with 30% H₂O₂ alone, with and without BTEAC

Cyclohexanone (0.2 ml, 1 mmol), dissolved in 20 ml of benzene was stirred at 55 °C with 20 ml of H₂O₂ for 24 h. The reaction was repeated in presence of BTEAC (100 mg). Yields of caprolactone were determined at 6 and 24 h (see Table 7).

Table 5. Effect of the amount of H₂O₂ on the yield of caprolactone

H ₂ O ₂ (ml)	Yield of caprolactone (%)	H ₂ O ₂ (ml)	Yield of caprolactone (%)
0.5	30.3	10	81.7
1	43.5	15	81.9
2	81.3	20	82.0
5	81.5		

Table 6. Effect of temperature and amount of H₂O₂ on the oxidation of ketones

Compound	H ₂ O ₂ (ml)	Temperature		Yield (%)	Compound	H ₂ O ₂ (ml)	Temperature		Yield (%)
		(°C)	Time				(°C)	Time	
Cyclohexanone	20	55	6 h	82	Cyclopentanone	40	80	3 h	100
Cyclohexanone	40	55	4 h	100	Camphor	40	80	5 h	75.3(α)
Cyclohexanone	20	80	2 h	100					24.7(β)
					Acetophenone	60	80	24 h	70.2
					Benzophenone	60	80	24 h	63

Table 7. Reaction of cyclohexanone with 30% H₂O₂ in the absence and presence of *BTEAC*

Time	Yield of caprolactone (%)	
	without <i>BTEAC</i>	with <i>BTEAC</i>
6 h	40	66
24 h	60	80

Formation of peroxy species of borax with polymeric persulfonic acid

Polymeric sulfonic acid (AG 50W-X8, Bio-Rad) was stirred with 30% H₂O₂ at room temperature for 6 h. The solution was decanted and the reaction with H₂O₂ was repeated 4–5 times. The resin was washed with distilled water until the washings failed to liberate iodine from acidified KI solution. At this stage, the polymer beads gave a strong colour with acidified KI solution. Borax (4 mmol, 1.5 g) dissolved in 20 ml H₂O was stirred with this polymer for 6 h at room temperature and filtered. Filtrate as well as polymer gave a positive result when checked for the liberation of iodine. The filtrate was mixed with cyclohexanone (1 mmol, 0.2 ml) in benzene (20 ml) and *BTEAC* (100 mg) and was heated at 55 °C for 48 h; the yield of caprolactone was 17.4%.

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