

p-ACETAMOL FROM PHENOL VIA p-NITROPHENOL

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ABSTRACT

p-Nitrophenol is obtained from phenol by nitrating phenol chemically and p-nitrophenol is then reduced to p-aminophenol electrochemically. Since p-aminophenol is fixed as a p-aminophenol sulphate, it is directly used for producing p-acetamol. Results of the three operations are discussed in this paper.

Key Words: p-acetamol, p-nitrophenol, Ti^{3+} / Ti^{4+} redox couple

INTRODUCTION

p-Acetamol is normally produced from p-nitrophenol (PNP) which, in turn, is produced by hydrolysis of p-chloronitrobenzene [1], and this is injurious to health. But PNP obtained from phenol is free from such contaminations. Good yield of nitrophenol is reported by nitrating phenol [2]. PNP thus obtained is reduced to p-aminophenol sulphate (PAPS) by electrolytic method [3], which has the following advantages over chemical method: (i) the purity of the product is maximum (ii) no other side product is formed (iii) pollution hazard will be minimum and (iv) quantitative yield can be achieved.

PAPS thus obtained can be directly acetylated as the loss can be minimised if it is handled as sulphate instead of free base. An attempt was made in an earlier communication by acetylating the wet free base p-aminophenol and the yield was 66.4% [4]. This paper highlights some improvements over earlier techniques by which the yield of p-acetamol was 86%.

Preparation of nitrophenol and aminophenol from phenol*Preparation of nitrophenol*

In a 500 ml lead vessel provided with a mechanical stirrer, 81 g sodium nitrate and 215 ml water was added and cooled with ice. Sulphuric acid (1.835) 73.3 ml, was added with stirring. 50 ml distilled phenol was added drop by drop while the temperature was maintained below 30°C and stirring continued for 2 1/2 hours after addition of phenol. The aqueous solution was steam distilled to recover o-nitrophenol (ONP) and the solution was kept for cooling so that PNP separates out. The non-aqueous portion was steam distilled and ONP was recovered. ONP thus obtained was dried and weighed. The solution in the still was made alkaline by adding sodium carbonate. Since sodium hydroxide has resinifying action with PNP, it was avoided. The solution containing PNP and sodium carbonate was treated with activated charcoal and the clear solution was made acidic with HCl when PNP separates out. It was recovered, dried and weighed. 23.6 g ONP (M.P., 45°C) and 29.5 g PNP (M.P. 114°C) were obtained, thus accounting an overall yield of 75%.

Preparation of aminophenol from nitrophenol

Electrolytic reduction of PNP to PAP can be done as per the procedure published earlier [3]. Conditions for reuse of electrolyte are shown below:

	Conditions
Catholyte	.. 900 ml 25% H_2SO_4 (v/v)
Anolyte	.. 200 ml
Titanium sulphate added to catholyte	.. 200 ml solution containing $Ti(SO_4)_2$ equivalent to 10.2 g TiO_2
Current density	.. 10 A.dm ⁻²
Cathode	.. Stationary copper of area 1.8 dm ²
Current	.. 18 A
Temperature	.. 50° - 55° C

Diaphragm
Voltage

.. Ceramic porous pot
.. 5.6 V

The same electrolyte was reused for more than six times and the overall yield as PAPS was 96.6%.

Preparation of p-acetamol from PAPS

100 g PAPS was mixed with ammonium bicarbonate, water and acetic anhydride with 0.5 g sodium bisulphate. The entire mixture was refluxed for not less than 2 hours and contents poured over 100 ml water. This solution was boiled to remove the excess acetic anhydride. It was then cooled, filtered and dried to obtain the p-acetamol. The yield varied from 73 to 88% for the three runs made as shown on Table I.

Table I: Preparation of p-acetamol from PAPS

No.	PAPS taken (g)	Ammo. bicarb. added (g)	Water added (ml)	(Ac) ₂ O added (ml)	Dry p-acetamol (g)	Yield %
1	100	50	190	80	70	73
2	100	50	100	80	75	78
3	100	50	100	75	86	88

CONCLUSION

Although a chemical method [5, 6] is available for the production of p-acetamol from phenol through p-nitrosophenol, its chemical conversion and then reduction with polysulfide brings down the yield considerably due to tarry side products. In the present method, p-nitrophenol, obtained by nitrating phenol, is reduced electrochemically to p-aminophenol, from which p-acetamol is prepared.

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