A green chemical approach for nitration of aromatic compounds

Arpita Dugar and Suresh C. Ameta*

Photochemistry Laboratory, Department of Chemistry, M. L. Sukhadia University, Udaipur-313 001, Rajasthan, India

E-mail: ameta_sc@yahoo.com

Manuscript received 6 March 2009, revised 12 August 2009, accepted 4 September 2009

Abstract: Photochemical aromatic nitration of anthranilic acid has been carried out in the presence of UV radiations and the formation of product has been observed spectrophotometrically. The effect of different variables like pH, concentration of nitrite ion, formate ion, anthranilic acid etc. was observed on the rate of the reaction. A tentative mechanism involving \( \text{NO}_2^- \) radicals has been proposed for photochemical nitration of anthranilic acid.

Keywords: Photochemical nitration, aromatic, eco-friendly.

Introduction

In several industrially important processes like nitration, nitrosation, etc. a large excess of sulfuric acid is required because the by-product water slows down the reaction by diluting the acid. At the end of these processes, a large amount of "spent acid" is obtained which, in batch reactions, is usually neutralized and disposed off, while, in continuous processes, it has to be recycled by complex techniques. Also, the separation of the products from the acid is often a difficult task and energy consuming process that habitually implies a basic aqueous work up. Moreover, sulfuric acid is corrosive in nature and is difficult to transport and handle and, therefore, it has been proposed to develop an alternate green chemical pathways to synthesize nitro compounds under ambient conditions.

The destruction of hazardous organic pollutant in waste streams, drinking water and industrial effluent can be achieved through the use of Advance Oxidation Technologies (AOT). These are chemical oxidation techniques, which are able to produce \textit{in situ} reactive free radicals, mainly hydroxyl radicals (\( \text{OH} \)) by means of different reacting systems. These processes are capable of degrading almost all organic contaminants. The concept of AOT was originally established by Glaze \textit{et al.} \cite{1} as "Oxidation Processes, which generated hydroxyl radicals in sufficient quantity to affect water treatment". Nitration of peptide phototoxin by bacterial nitric oxide synthase was reported by Brian \textit{et al.} \cite{2}. Nitration of many organic compounds using different nitrating agents like nitroso-benzene, nitric acid, \( \text{Zn(NO}_3\text{)}_2 \), 2.\( \text{N}_2\text{O}_4 \), nitrate and nitrite ions are reported earlier\cite{3-14}, but these are associated with some of the other demerits, and hence, can not be considered as an eco-friendly approach.

Experimental

0.1370 g of anthranilic acid was dissolved in 100 ml of doubly distilled water. 0.0690 g of \( \text{NaNO}_2 \) and 0.0680 g of sodium formate were dissolved separately in 100 ml of doubly distilled water. All the three solutions were used as stock solutions. 6.0 ml of anthranilic acid solution, 8.0 ml of \( \text{NaNO}_2 \) solution and 0.7 ml of sodium formate solution were mixed, so that the concentrations of anthranilic acid, sodium nitrite and sodium formate in the solution were 2.4 \( \times 10^{-3} \) \( M \), 3.2 \( \times 10^{-3} \) \( M \) and 2.8 \( \times 10^{-4} \) \( M \) respectively.

The reaction mixture was exposed to ultraviolet lamp (254 nm). The optical density of this solution at various time intervals was determined at \( \lambda_{\text{max}} = 380 \) nm for anthranilic acid with the help of spectrophotometer (Systronic Model 106). Some control experiments were also carried out and it was concluded as light is necessary.
for photochemical nitration of anthranilic acid. The products were identified by gas chromatography combined with mass spectroscopy GC-MS (Perkin-Elmer Auto system XL).

Results and discussion

The results of a typical run for photochemical nitration are shown in Table 1. It was observed that absorbance increases with time of exposure, which indicates the formation of nitro products: A plot of $1 + \log A$ versus exposure time was linear and hence, this reaction follows pseudo-first order kinetics (in two stages; the first stage being faster than the second stage). The rate constant was determined by the expression $k = 2.303 \times \text{slope}$.

Effect of pH:

The pH of medium is likely to affect the rate of reaction. Effect of pH on reaction rate was investigated in the pH range of 6.0–8.5 and the results are summarized in Table 2. The rate of reaction increases on increasing pH up to 7. Thereafter, there is an adverse effect on the rate of reaction on increasing the pH, further.

Initially, when pH was increased, the reaction rate also increases because $N_2O_4$ and $N_2O_3$ are easily generated.

\[
N_2O_3 + ArH \rightarrow ArNO + NO_2^- + H^+ \quad (3)
\]

\[
\text{Oxidation}
\]

\[
ArNO \rightarrow ArNO_2 \quad [\text{O}] \quad (4)
\]

\[
N_2O_4 + ArH \rightarrow ArNO_2 + NO_2^- + H^+ \quad (5)
\]

Retardation of rate by further increase in pH may be due to reduced generation of $NO_2^*$ radicals.

\[
*OH + NO_2^- \rightarrow NO_2^* + OH^- \quad (6)
\]

As any increase in pH will add more $OH^-$ ions to the solution and therefore, will retard the reaction (6) and as a consequence, the formation of $NO_2^*$ radicals also. Hence, there will be a corresponding decrease in the rate of reaction.

Table 1. A typical run for anthranilic acid

| Time (min) | $1 + \log A$ |
|-----------|---------------|
| 3.0       | 0.4996        |
| 6.0       | 0.5094        |
| 9.0       | 0.7249        |
| 12.0      | 0.8182        |
| 15.0      | 0.8981        |
| 18.0      | 0.9812        |
| 21.0      | 1.0560        |
| 24.0      | 1.1003        |
| 27.0      | 1.1150        |
| 30.0      | 1.1390        |
| 33.0      | 1.1470        |
| 36.0      | 1.1528        |
| 39.0      | 1.1672        |
| 42.0      | 1.1744        |
| 45.0      | 1.1878        |
| 48.0      | 1.1969        |
| 51.0      | 1.2098        |
| 54.0      | 1.2113        |
| 57.0      | 1.2132        |
| 60.0      | 1.2178        |
| 63.0      | 1.2231        |
| 66.0      | 1.2232        |

$\text{Effect of nitrite ion concentration :}$

Effect of nitrite ion concentration on the rate of reaction was also investigated and the results are given in Table 2. It was observed that rate of reaction increases with the increase in nitrite ion concentration up to certain limit i.e. $3.2 \times 10^{-3} \text{ M}$. After this, a further increase in concentration of nitrite ion affects the rate of reaction adversely.

As the concentration of sodium nitrite was increased, more $NO_2^-$ ions were available for excitation and consecutive generation of $NO_2^*$ radicals and hence, rate of reaction increases but after a certain limit, these nitrite ions will hinder their own movement, which in turn, will decrease the rate of reaction.
Effect of formate ion concentration:

As the formate ions are known OH\(^{-}\) radical scavenger and therefore, the photochemical nitration has been carried out in the presence and absence of formate ions. It was observed that the rate of photochemical reaction increases rapidly in the presence of formate ions. It is because of the fact that OH\(^{-}\) radicals are scavenged by formate ions, thus, leaving, more NO\(_2\)\(^{-}\) radicals for nitration. Moreover, OH\(^{-}\) radicals also decrease the concentration of NO\(_2\)\(^{-}\) radicals according to eq. (8). The results are reported in Table 3.

\[
\text{HCOO}^- + \cdot \text{OH} \rightarrow \text{CO}_2^- + \text{H}_2\text{O}
\]  
(7)

\[
\text{OH}^- + \text{NO}_2^- \rightarrow \text{NO}_3^- + \text{H}^+
\]  
(8)

Effect of anthranilic acid concentration:

Effect of change in concentration of anthranilic acid on the rate of reaction are presented in Table 3.

Identification of products:

The major products was identified as 1 \([M^+ = 198.7]\).

Although formate ions were used as \(^{\cdot}\)OH radical scavengers in order to increase the rate of nitration, but since \(^{\cdot}\)OH radicals are very reactive and higher in concentration than NO\(_2\)\(^{-}\) radicals; therefore \(^{\cdot}\)OH groups is also introduced in the ring even in the presence of formate ions. Nitroso group (-NO) has also been introduced into the ring.

Two minor products were also obtained and characterized by GC-MS as 2 and 3.
Mechanism:

On the basis of the observed data, a tentative mechanism has been proposed for the nitration of anthranilic acid.

\[
\text{NO}_2^- \xrightarrow{\text{hv}} [\text{NO}_2^-]^* \\
[\text{NO}_2^-]^* \rightarrow \text{NO}^+ + \text{O}^- \\
\text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}^- \\
2\text{OH} + \text{NO}^+ \rightarrow \text{NO}_2^* + \text{H}_2\text{O} \\
\text{OH} + \text{NO}_2^- \rightarrow \text{NO}_2^* + \text{OH}^- \\
\]

where \( R = -\text{OH} \) and \( R' = -\text{H} \) (in phenol) and \( R = -\text{COOH} \) and \( R' = -\text{OH} \) (in salicylic acid).

Nitrite ion absorbs radiation of suitable wavelength and gets excited. This excited nitrite ion dissociates into \( \text{NO}^* \) radicals and \( \text{O}^- \) radical anion. This radical anion decomposes water to give \( \text{OH}^* \) radicals and \( \text{OH}^- \) ion. The \( \text{OH}^* \) radical may react with \( \text{NO}^* \) radical to generate \( \text{NO}_2^* \) radical, which may also undergo in cage recombination reaction giving nitrite ion. This step seems to dominate in higher pH range. These \( \text{NO}_2^* \) radicals now attack the aromatic moiety giving nitro derivatives. Nitroso and hydroxyl derivatives (minor products) are obtained by the attack of \( \text{NO}^* \) and \( \text{OH}^* \) radicals on anthranilic acid, respectively.

Conclusion:

Ordinary nitration of aromatic systems is accompanied by hazardous brown fumes of \( \text{NO}_2 \) gas, which adds to environmental pollution. The present work provides a facile route for this process i.e. nitration. However, the yield of the product is not reached to the desired extent, but photochemical nitration of aromatic systems by alkali nitrates will provide an eco-friendly route and the rate of the reaction may be increased in years to come to make this process commercially viable.

Acknowledgement

Authors are thankful to the Head of the Chemistry Department, Mohanlal Sukhadia University, Udaipur, for providing laboratory facilities.

References

1. W. H. Glaze, J. W. Kang and D. H. Chapin, Ozone Sci. Engg., 1987, 9, 335.
2. R. B. Crane, M. D. Gibson, B. S. Krasnoff and L. R. Loria, J. Biol. Chem., 2004, 429, 79.
3. V. M. Nagaev, G. A. Sorol Skii, S. S. Khokhlov and A. F. Eleev, Russ. Chem. Bull., 2003, 52, 2285.
4. Y. Kono, Biosci. Biotechnol. Biochem., 1998, 62, 448.
5. N. Matykiewicezova, R. Kurkova, J. Kluanova and P. Klan, J. Photochem. Photobiol., 2007, 187A, 24.
6. D. L. Liptin, A. M. Churakov, S. L. Ioffe, Y. A. Streleuko and V. A. Tartakovksy, Eur. J. Org. Chem., 1999, 1, 29.
7. K. Smith, A. Musson and G. A. De Boss, J. Org. Khim., 1998, 63, 8448.
8. J. M. Bakke, H. Svensen and E. Ranes, J. Chem. Soc., Perkin Trans. 2, 1998, 11, 2477.
9. S. P. Dageade, S. B. Wagmode, V. S. Kadarn and M. K Dongre, Appl. Catal., 2002, 202, 49.
10. F. Badea, A. Stoica, P. Lonita, M. T. Capiu and T. Constantescu, Rev. Roum. Chim., 2000, 19, 492.
11. J. M. Mellor, R. Parkes and R. W. Millar, Tetrahedron, 1997, 38, 8739.
12. T. Ohta, J. Suzuki, Y. Iwano and S. Suzuki, Chemosphere, 1982, 11, 797.
13. N. Iranpour, H. Firouzabadi and R. Heyderi, Synthetic Commun., 2005, 35.
14. S. Nelieu, L. Kerhoas and M. V. Einhorn, J. Photochem. Photobiol., 2008, 193, 1.