Research Article

The Oxidation of 2,4,6-Trinitrotoluene with an Ozone-Oxygen Mixture: A Simple Method for Preparation of 1,3,5-Trinitrobenzene

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The oxidation of 2,4,6-trinitrotoluene (TNT) to 1,3,5-trinitrobenzene (TNB) in one step, 2,4,6-trinitrobenzoic acid (TNBA), and 2,4,6-trinitrobenzaldehyde (TNBAL) with an ozone-oxygen mixture in different solvents, catalysts, and temperatures has been investigated. Reducing the number of steps in the oxidation of TNT to TNB is the major advantage of this procedure with respect to conventional processes such as chromic acid and potassium permanganate. The oxidation of TNT to TNB was completed in one step as compared to two steps in the conventional approach. The products were obtained with relatively good yield.

1. Introduction

1,3,5-Trinitrobenzene (TNB) is an explosive compound with slightly greater explosive force than 2,4,6-trinitrotoluene (TNT) [1]. TNB is used primarily as a high explosive for commercial mining and military use. Also, it has been employed as an agent to vulcanize natural rubber [2] and as a mediating agent to mediate the synthesis of other explosive compounds [3].

So far, the different methods for preparation of TNB were reported [4–8]. The most common method is the oxidation of TNT to TNB using oxidants such as chromic acid, potassium permanganate in acid, basic, and neutral solutions, nitric acid, and silver oxide in which these methods are not attractive because they produce the large amounts of toxic and difficultly utilizable wastes. On the other hand, direct nitration of benzene requires such harsh conditions whose yields are poor, and purification of TNB is very difficult. Even the use of modern catalysts such as lanthanide nitrates does not alleviate this problem [9].

In this paper, we investigated the one-step oxidation of TNT with an ozone-oxygen mixture in presence of the different conditions such as catalyst, temperature, and oxidative

agents (Table 1). In addition, this method can be used to develop a low-waste process for TNB production. Also, this reaction is carried out with 2,4-dinitrotoluene (DNT) to prove the generality of this procedure (Table 2). The obtained results approximately were similar to each other. Synthesis route of the reactions is shown in Figure 1.

2. Experimental

Materials were purchased from Merck and Fluka companies. ¹HNMR spectra were recorded with a Bruker DRX-300 Avance instrument using CDCl₃ as the deuterated solvent containing tetramethylsilane as internal standard, at 300, δ in parts per million, and J in hertz. The experiments were carried out with a Compact Ozone Generator (OZONEUF, model: COG 10 S). Elemental analyses (C, H, and N) were obtained with a Heraeus CHN–O– Rapid analyzer.

2.1. Typical Procedure without Hydrogen Peroxide. TNT or DNT was oxidized in a round-bottom flask (100 mL) with a fine-pore barrier for dispersion of the gas mixture. The reactor was charged with TNT or DNT (4 mmol), catalyst (1 mmol), KBr (0.1 g), and 40 mL of glacial acetic acid

TABLE 1: The conditions and results of the oxidation of TNT.

Entry ²	Solvent	Co(OAc) ₂ ·4H ₂ O	Temperature (°C)	Co(NO ₃) ₂ ·6H ₂ O	H ₂ O ₂ (%30)	%TNBAI	%TNBA	%TNB
1	CH ₃ COOH	1 mmol	40			10	0	0
2	CH ₃ COOH	1 mmol	100			60	0	0
3	CH ₃ COOH	1 mmol	40		20 mL	27	0	0
4	CH ₃ COOH	1 mmol	100		20 mL	68	23	0
5	HCOOH	1 mmol	40			23	0	0
6	HCOOH	1 mmol	100			45	36	0
7	HCOOH	1 mmol	40		20 mL	40	15	35
8	HCOOH	1 mmol	100		20 mL	15	0	74
9	CH ₃ COOH		40	1 mmol		12	0	0
10	CH ₃ COOH		100	1 mmol		57	0	0
11	CH ₃ COOH		40	1 mmol	20 mL	28	0	0
12	CH ₃ COOH		100	1 mmol	20 mL	60	30	0
13	HCOOH		40	1 mmol		18	0	0
14	HCOOH		100	1 mmol		53	32	0
15	HCOOH		40	1 mmol	20 mL	34	21	18
16	HCOOH		100	1 mmol	20 mL	24	5	65

²The time of ozonolysis for all reactions was 6 h.

TABLE 2: The conditions and results of the oxidation of DNT.

Entry ³	Solvent	Co(OAc) ₂ ·4H ₂ O	Temperature (°C)	Co(NO ₃) ₂ ·6H ₂ O	H ₂ O ₂ (%30)	%DNBAI	%DNBA	%DNB
1	CH ₃ COOH	1 mmol	40			27	0	0
2	CH ₃ COOH	1 mmol	100			74	0	0
3	CH ₃ COOH	1 mmol	40		20 mL	45	0	0
4	CH ₃ COOH	1 mmol	100		20 mL	73	18	0
5	HCOOH	1 mmol	40			31	0	0
6	HCOOH	1 mmol	100			28	57	0
7	HCOOH	1 mmol	40		20 mL	29	21	38
8	HCOOH	1 mmol	100		20 mL	0	12	86
9	CH ₃ COOH		40	1 mmol		34	0	0
10	CH ₃ COOH		100	1 mmol		66	0	0
11	CH ₃ COOH		40	1 mmol	20 mL	43	0	0
12	CH ₃ COOH		100	1 mmol	20 mL	51	43	0
13	HCOOH		40	1 mmol		32	0	0
14	HCOOH		100	1 mmol		26	51	0
15	HCOOH		40	1 mmol	20 mL	31	25	42
16	HCOOH		100	1 mmol	20 mL	0	16	73

³The time of ozonolysis for all reactions was 6 h.

FIGURE 1: Synthesis route of DNT and TNT oxidation. Only the major product is shown.

or formic acid. Then it was stirred and heated to the required temperature, and an ozone-oxygen mixture was fed for 6 h. Afterwards, the mixture of reaction is mixed with 500 g of crushed ice. Then the produced precipitation was purified by column chromatography (SiO_2 ; n-hexane/AcOEt = 5/1) to afford the pure adducts.

2.2. Typical Procedure with Hydrogen Peroxide. TNT or DNT was oxidized in a round-bottom flask (100 mL) with a fine-pore barrier for dispersion of the gas mixture. The reactor was charged with TNT or DNT (4 mmol), catalyst (1 mmol), KBr (0.1 g), 40 mL of glacial acetic or formic acid, and 10 mL (H_2O_2 %30). Then it was stirred and heated to the required temperature, and an ozone-oxygen mixture was fed. After 2 h ozonolysis, 10 mL H_2O_2 again was added to the mixture of reaction. Afterwards, the mixture of reaction is mixed with 500 g of crushed ice. Then the produced precipitation was purified by column chromatography (SiO_2 ; n-hexane/AcOEt = 5/1) to afford the pure adducts.

3. Data

2,4,6-Trinitrobenzaldehyde. Yield: 68%, yellow powder, mp 119°C [lit. [10] mp 119°C]. IR (KBr) ($\nu_{\text{max}} = \text{cm}^{-1}$): 3092 (CH), 2859 (CH aldehyde), 1696 (C=O), 1587 (C=C), 1529 and 1349 (NO_2). Anal. Calcd. for $\text{C}_7\text{H}_3\text{N}_3\text{O}_7$ (241.00): C, 34.87; H, 1.25; N, 17.43; Found: C, 34.6; H, 1.2; N, 17.5. ^1H NMR (300 MHz, CDCl_3): 8.85 (s, 2H), 10.33 (s, 1H).

2,4,6-Trinitrobenzoic Acid. Yield: 36%, yellow powder, mp 229°C . IR (KBr) ($\nu_{\text{max}} = \text{cm}^{-1}$): 3110 (OH), 3086 (CH), 1712 (C=O), 1609 (C=C), 1549 and 1369 (NO_2). Anal. Calcd. for $\text{C}_7\text{H}_3\text{N}_3\text{O}_7$ (256.99): C, 32.70; H, 1.18; N, 16.34; Found: C, 32.8; H, 1.1; N, 16.6. ^1H NMR (300 MHz, CDCl_3): 9.13 (s, 2H), 11.1 (s, 1H).

1,3,5-Trinitrobenzene. Yield: 74%, yellow sludgy powder, mp 123°C [lit. [4, 11, 12] mp $121\text{--}122^\circ\text{C}$]. IR (KBr) ($\nu_{\text{max}} = \text{cm}^{-1}$): 3107 (CH), 1623 (C=C), 1544 and 1345 (NO_2). Anal. Calcd. for $\text{C}_6\text{H}_3\text{N}_3\text{O}_6$ (213.00): C, 33.82; H, 1.42; N, 19.72; Found: C, 33.6; H, 1.5; N, 19.9. ^1H NMR (300 MHz, CD_3COCD_3): 9.33 (s, 3H).

2,4-Dinitrobenzaldehyde. Yield: 73%, yellow crystal, mp 73°C [lit. [10, 13] mp $69\text{--}72^\circ\text{C}$]. IR (KBr) ($\nu_{\text{max}} = \text{cm}^{-1}$): 3111 (CH), 2877 (CH aldehyde), 1701 (C=O), 1601 (C=C), 1537 and 1360 (NO_2). Anal. Calcd. for $\text{C}_7\text{H}_4\text{N}_2\text{O}_5$ (196.12): C, 42.87; H, 2.06; N, 14.28; Found: C, 42.6; H, 2.02; N 14.15. ^1H NMR (300 MHz, CDCl_3): 8.34 (s, 1H), 8.14 (d, 1H), 8.03 (d, 1H), 10.32 (s, 1H).

2,4-Dinitrobenzoic Acid. Yield: 57%, yellow crystals, mp 181°C [lit. [14] mp $182\text{--}183^\circ\text{C}$]. IR (KBr) ($\nu_{\text{max}} = \text{cm}^{-1}$): 3122 (OH), 3084 (CH), 1724 (C=O), 1620 (C=C), 1544 and 1356 (NO_2). Anal. Calcd. for $\text{C}_7\text{H}_4\text{N}_2\text{O}_6$ (212.12): C, 39.64; H, 1.90; N, 13.21; Found: C, 39.5; H, 1.8; N, 13.4. ^1H NMR (300 MHz, CDCl_3): 8.65 (d, 1H), 8.48 (dd), 8.06 (d, 1H), 10.8 (s, 1H).

1,3-Dinitrobenzene. Yield: 86%, yellow powder, mp 91°C [lit. [12] mp $89\text{--}90^\circ\text{C}$]. IR (KBr) ($\nu_{\text{max}} = \text{cm}^{-1}$): 3110 (CH), 1615

(C=C), 1538 and 1364 (NO_2). Anal. Calcd. for $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$ (168.11): C, 42.87; H, 2.40; N, 16.66; Found: C, 42.7; H, 2.3; N, 16.4. ^1H NMR (300 MHz, CDCl_3): 8.79 (t, 1H), 8.62 (dd, 2H), 7.96 (t, 1H).

4. Results and Discussion

According to Table 1, the reaction of ozone with TNT in different conditions leads to the diverse products such as TNBAL, TNBA, and TNB. As it is observed, the temperature plays an important role in the ozonolysis reaction. At 40°C , the reaction of ozone with TNT in presence of $\text{Co}(\text{OAc})_2$ was slow, and the conversion reached 10% after 6 hours (entry 1). At 100°C , TNBAL yield based on the reacted substrate reaches 60% (entry 2). Also, it is characterized that if the time and temperature of ozonolysis increase (12 h, 100°C), the reaction yield reaches 0%. This shows that the reaction with cleavage of aromatic ring forwarded which could be degraded gradually into final products such as aliphatic organic acids, water, and carbon dioxide [15, 16]. The addition of hydrogen peroxide to pervious reactions causes acceleration of the oxidation and the increase of yield at 100°C (TNBAL 68% and TNBA 23%). When the reaction is carried out in formic acid and hydrogen peroxide, the obtained results were remarkable. At 100°C , TNB as the major product (74%) obtained which it is the favorable method for synthesis this compound. Also, according to Table 1, the obtained results with $\text{Co}(\text{NO}_3)_2$ almost were similar to $\text{Co}(\text{OAc})_2$ (entries 9–16). On the other hand, the oxidation of DNT is carried out to prove the generality of this method. According to Table 2, it could be found that the results approximately are the same to TNT oxidation which confirms this efficient procedure for other substituted toluenes.

Only, the mechanism which we have suggested to correlate all the results of this work involves the presence of the free radicals of hydroxyl and perhydroxyl as intermediates in these homogeneous reactions. A plausible mechanism for the formation of products is shown in Figure 2. Under the experimental conditions, ozone oxidizes mainly Co^{2+} to reactive Co^{3+} species (1) which rapidly and selectively oxidize the methyl group of aryl (2). In the presence of H_2O_2 , after the ozone undergoes a catalytic decomposition by Co^{+2} , the mixture of Co^{+3} and ozone is added to hydrogen peroxide in which the reaction between Co^{+3} and hydrogen peroxide induces a decomposition of ozone by reactions (4) and (5). The produced free radicals, hydroxyl and perhydroxyl ones, will start a chain decomposition by reactions (4) and (5). The presence of these radicals previously has been reported [17, 18]. Then, the produced benzyl radical (2, 6) is attacked by O_2 to produce peroxide and aldehyde. Also, the subsequent reaction with ozone or hydrogen peroxide results in TNBA or TNB.

Introduction of potassium bromide into the reaction mixture substantially accelerates the oxidation with an ozone-oxygen mixture [19]. The suggested mechanism is that potassium bromide reacts with cobalt (II) to form $\text{Co}^{2+}\text{Br}^-$ in which this complex is more reactive than Co^{3+} and oxidizes TNT by the reaction shown in Figure 3.

FIGURE 2: Plausible mechanism for the formation of products.

FIGURE 3

5. Conclusion

The yields of TNB and DNB in this procedure were obtained as 74% and 86%, respectively. Also, this method can be used to produce TNB and DNB for applied future.

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