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Using x-ray diffraction for probing the structure of ethylen bispyridinium peroxodisulfate (EBPPD) as a new oxidant

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ABSTRACT

Ethylen Bispyridinium PeroxoDisulfate (EBPPD) is prepared by addition of pyridine to 1,2-dibromoethane to form the corresponding dibromide salt and subsequent addition of this aqueous solution to a solution of Potassium Peroxodisulfate in water. The structure of EBPPD has been probed by Crystallographic X-Ray analysis. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Ethylen bispyridinium peroxodisulfate;
Crystallographic x-ray;
Analysis;
Bispyridinium bromide;
Potassium peroxodisulfate.

INTRODUCTION

The availability of selective oxidants for selective functional group transformation of organic compounds is of obvious importance to research in organic chemistry. Peroxodisulfate in several cases fulfills most requirements^[1]. The peroxodisulfate ion, $S_2O_8^{2-}$, is one of the strongest oxidizing agents and is even stronger than H_2O_2 . The standard redox potential is estimated to be 2.01V (1.77 for H_2O_2) in aqueous solution^[2]. $S_2O_8^{2-}$ oxidation frequently proceeds by an initial O-O bond breakage to give, the radical anion $SO_4^{\cdot-}$, which appears to be a very effective electron transfer oxidizing agent^[1]. Many standard oxidation procedures have been available for this purpose. The selective oxidation of varieties of organic compounds is an important transformation because of the complexities in natural product structures, and many methods have been developed to accomplish this particular reaction^[3-7]. Although the various methods have some synthetic advantages indi-

vidually, they still suffer from one or more drawbacks such as, low yield, harsh or delicate reaction condition, the need for large excess of oxidant and side reactions. Therefore, it is still important to develop a selective, mild and efficient method. In recent years new peroxodisulfate oxidants such as tetrakis (pyridine) silver (II) peroxodisulfate ($[Ag(py)_4] S_2O_8$)^[8], benzyl triphenyl phosphonium peroxodisulfate ($[PhCH_2PPh_3]_3 S_2O_8$)^[9], n-butyl triphenyl phosphonium peroxodisulfate ($[n-BupPh_3]_2 S_2O_8$)^[10], bis (1-benzyl -4-aza-1-azoniabicyclo [2.2.2] octane) peroxodisulfate^[11], Cetyltrimethyl ammonium peroxo disulfate^[12,13], bis(bipyridine) silver (II) peroxy disulfate and potassium peroxo disulfate^[14] have been used for oxidation varieties of organic substrates.

In connection with our ongoing program to find new oxidizing agents for organic substrates, we have found that Ethylene Bispyridinium Peroxodisulfate (EBPPD) is an efficient and more stable and so bench top oxidant for oxidation of varieties organic compounds.

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X-ray crystallography

Suitable single crystals of (**1**) were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a Nonius DIP1030H system with graphite-monochromated Mo-K α radiation ($\lambda=0.71073$ Å) at 298(2) K. Cell refinement, indexing and scaling of the data set were carried out using packages Denzo and Scalepack^[15]. The structure were solved by direct methods and refined by full-matrix least-squares methods on F^2 by using the SHELX-97 program package^[16]. The weighting scheme was $w = 1/[\sigma^2(FO^2) + (0.0474P)^2]$ where $P = (FO^2 + 2Fc^2)/3$. The contribution of H atoms at calculated position was introduced in the final cycles of refinement. All the calcula-

TABLE 1 : Crystallographic data and structure refinement parameters of 1

Empirical formula	: C ₁₂ H ₁₄ N ₂ O ₈ S ₂
Formula weight	: 378.37
Temperature	: 298(2) K
Wavelength	: 0.71073 Å
Crystal system	: Monoclinic
Space group	: $P 2_1/c$
Unit cell dimensions	: $a = 8.201(4)$ Å, $b = 9.861(3)$ Å, $c = 9.933(2)$ Å
Volume	: $\alpha = 90^\circ$, $\beta = 98.36(3)^\circ$, $\gamma = 90^\circ$
Z, Calculated density	: $794.8(4)$ Å ³
Absorption coefficient	: 2, 1.581 Mg/m ³
F(000)	: 0.380 mm ⁻¹
Crystal size	: 392
Theta range for data collection	: 0.4 x 0.2 x 0.15 mm
Index ranges	: 3.66 to 29.62°
Reflections collected / unique	: $-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-13 \leq l \leq 13$
Observed reflections [I>2 σ (I)]	: 8970 / 2129 [R(int) = 0.0337]
Completeness to theta = 29.62°	: 1864
Max. and min. transmission	: 94.7 %
Refinement method	: Full-matrix least-squares on F^2
Data / restraints / parameters	: 2129 / 0 / 110
Goodness-of-fit on F^2	: 1.090
Final R indices [I>2 σ (I)]	: R1 = 0.0417, wR2 = 0.1246
R indices (all data)	: R1 = 0.0452, wR2 = 0.1269
Absolute structure parameter	: 0.16(2)
Largest diff. peak and hole	: 0.203 and -0.316 e.Å ⁻³

tions were performed using the WinGX System, Ver 1.80.05^[17]. The crystallography details for the structures determination of (**1**) was presented in TABLE 1. Atomic coordinates and equivalent isotropic displacement parameters, bond distances and bond angles and anisotropic displacement parameters are listed in TABLE 2, TABLE 3 and TABLE 4, respectively.

TABLE 2 : Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for (1). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	8392(2)	5689(1)	5973(1)	48(1)
C(1)	7635(2)	4936(2)	6820(2)	55(1)
C(2)	6106(2)	5305(2)	7103(2)	62(1)
C(3)	5351(2)	6449(2)	6512(2)	65(1)
C(4)	6150(2)	7217(2)	5640(2)	68(1)
C(5)	7684(2)	6818(2)	5382(2)	60(1)
C(6)	10062(2)	5306(2)	5710(2)	52(1)
S(1)	1633(1)	8821(1)	4268(1)	50(1)
O(1)	2848(2)	9446(2)	3571(2)	72(1)
O(2)	2233(2)	8189(2)	5545(1)	71(1)
O(3)	415(2)	8020(1)	3437(1)	64(1)
O(4)	682(2)	10211(1)	4631(2)	67(1)

TABLE 3 : Bond lengths [Å] and angles [°] for 1.

N(1)-C(1)	1.341(2)
N(1)-C(5)	1.349(2)
N(1)-C(6)	1.4800(19)
C(1)-C(2)	1.374(2)
C(1)-H(1)	0.9300
C(2)-C(3)	1.376(2)
C(2)-H(2)	0.9300
C(3)-C(4)	1.384(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.378(2)
C(4)-H(4)	0.9300
C(5)-H(5)	0.9300
C(6)-C(6)#1	1.523(3)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
S(1)-O(1)	1.4325(14)
S(1)-O(2)	1.4342(13)
S(1)-O(3)	1.4367(13)
S(1)-O(4)	1.6431(12)
O(4)-O(4)#2	1.482(2)
C(1)-N(1)-C(5)	121.41(13)

C(1)-N(1)-C(6)	119.58(14)
C(5)-N(1)-C(6)	118.98(13)
N(1)-C(1)-C(2)	120.09(15)
N(1)-C(1)-H(1)	120.0
C(2)-C(1)-H(1)	120.0
C(1)-C(2)-C(3)	119.81(16)
C(1)-C(2)-H(2)	120.1
C(3)-C(2)-H(2)	120.1
C(2)-C(3)-C(4)	119.40(16)
C(2)-C(3)-H(3)	120.3
C(4)-C(3)-H(3)	120.3
C(5)-C(4)-C(3)	119.24(16)
C(5)-C(4)-H(4)	120.4
C(3)-C(4)-H(4)	120.4
N(1)-C(5)-C(4)	120.05(15)
N(1)-C(5)-H(5)	120.0
C(4)-C(5)-H(5)	120.0
N(1)-C(6)-C(6)#1	109.03(15)
N(1)-C(6)-H(6A)	109.9
C(6)#1-C(6)-H(6A)	109.9
N(1)-C(6)-H(6B)	109.9
C(6)#1-C(6)-H(6B)	109.9
H(6A)-C(6)-H(6B)	108.3
O(1)-S(1)-O(2)	116.19(10)
O(1)-S(1)-O(3)	115.67(9)
O(2)-S(1)-O(3)	112.91(9)
O(1)-S(1)-O(4)	97.65(8)
O(2)-S(1)-O(4)	106.32(8)
O(3)-S(1)-O(4)	105.79(8)
O(4)#2-O(4)-S(1)	106.91(11)

Symmetry codes: #1 $-x + 2, -y + 1, -z + 1$; #2 $-x, -y + 2, -z + 1$

TABLE 4 : Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (1). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
N (1)	45(1)	49(1)	52(1)	-3(1)	13(1)	2(1)
C (1)	54(1)	56(1)	56(1)	6(1)	16(1)	6(1)
C (2)	55(1)	68(1)	67(1)	11(1)	24(1)	4(1)
C (3)	52(1)	72(1)	75(1)	6(1)	22(1)	12(1)
C (4)	62(1)	58(1)	89(1)	14(1)	24(1)	14(1)
C (5)	58(1)	52(1)	75(1)	9(1)	23(1)	3(1)
C (6)	43(1)	61(1)	54(1)	-7(1)	11(1)	2(1)
S (1)	46(1)	50(1)	54(1)	-1(1)	13(1)	7(1)
O (1)	60(1)	77(1)	88(1)	-6(1)	37(1)	-3(1)
O (2)	69(1)	78(1)	62(1)	8(1)	1(1)	16(1)
O (3)	66(1)	65(1)	59(1)	-7(1)	8(1)	-6(1)
O (4)	63(1)	44(1)	104(1)	5(1)	46(1)	3(1)

RESULTS AND DISCUSSION

The compound (1) crystallizes in the Monoclinic space group $P 2_1/c$. The structure of compound (1) is shown in Figure 1.

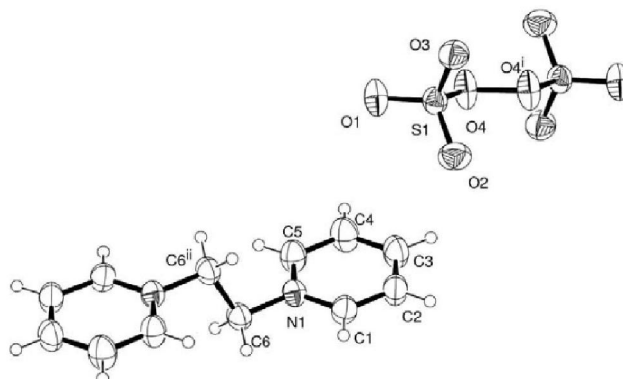


Figure 1 : ORTEP drawing at 40% probability ellipsoid of compound (1).

Both the ions are located on a crystallographic center of symmetry at the midpoint of C6-C6ⁱ and O4-O4ⁱ, respectively. The cell packing of the unit cell of compound (1) is shown in Figure 2.

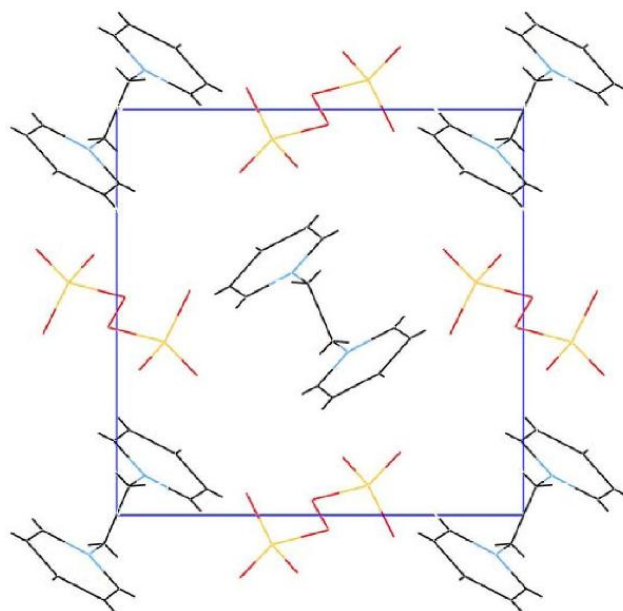


Figure 2 : A packing diagram of the unit cell of compound 1 looking down the a-axis.

EXPERIMENTAL SECTION

All the substrates were purchased from Fluka and Merck. The product were identified by X-Ray Crystallographic analysis and so ¹HNMR, IR spec-

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tra were measured at 100 MHz with a AC Bruker spectrometer with tetramethylsilane as an internal reference and D₂O as solvent. IR spectra were recorded with a FT IR 8400 s SHIMADZU (400-4000cm⁻¹) Spectrometer.

Preparation of ethylene bispyridinium peroxodisulfate (EBPPD)

A mixture of pyridine (4 ml, 44.8 mmol) and 1,2-dibromoethane (1.9 ml, 22mmol) was stirred in DMF (40 ml) at 120 °C for 2 h. After cooling the mixture, the white solid formed was filtered, washed with diethyl ether (3×25ml) and dried under vacuum^[18]. Then to a solution of EthylenBis pyridinium Bromide (10mmole, 3.43g) In 75 ml water K₂S₂O₈ (1.3g, 5 mmol) in 100 ml of water was added dropwise and the reaction mixture was stirred for 20min. at room temperature. A white solid was formed. The precipitate was filtered, washed with cold distilled water (50ml) And dried in a desicator under vacuum over calcium chloride to afford a white powder. The yield of EBPPD was 75% and decomposes at 200°C to a light brown material.

Ethylen bispyridinium peroxodisulfate: IR (KBr): (3120, W), (3080, M), (2380, M), (1640, M), (1490, S), (1270, S), (1200, S), (1090, S), (940, S), (790, S), (680, S), (530, S), (480, M), (430, W) cm⁻¹.

Ethylen bispyridinium peroxodisulfate: ¹H NMR (100 MHz, D₂O): δ 8.6(d, 4H, 4CH ortho), 8.45 (d, 2H, 2CH para), 8 (t, 4H, 4CH metha), 5.15(s, 4H, 2CH₂).

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