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In alkaline media, Fremy's salt oxidizes alkanols by a hydrogen atom transfer mechanism

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ABSTRACT

In aqueous alkali, Fremy's salt (potassium nitrosodisulfonate dimer), homolyses nearly exclusively to the monomer radical anion, nitrosodisulfonate (NDS). In this media, NDS almost quantitatively oxidizes benzyl alcohol (PhCH₂OH) to benzaldehyde (PhCHO), itself being reduced to hydroxylamine disulfonate (HNDS). The reaction is very nearly first-order in [NDS], [alkanol] and in [OH⁻]. However, with progressive addition of HNDS, decay kinetics of NDS gradually deviates from first-order. Ultimately, with sufficient excess of HNDS, the reaction becomes second-order in [NDS]. The consumption ratio, (Δ PhCH₂OH]/ Δ [NDS]), is ~2. PhCD₂OH manifests a large primary kinetic isotope effect ($k_H/k_D = 11.6$). Substituted benzyl alcohols (RBzCH₂OH) with R-groups withdrawing electron density from the O–H bond accelerated the reaction; those with R-groups donating electron density to the O–H bond retarded the reaction. The conversion of 2-propanol to 2-propanone is much slower compared to that of benzyl alcohol to benzaldehyde. An alpha-H atom transfer mechanism seems logical.

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1. Introduction

Fremy's salt (potassium nitrosodisulfonate dimer) is a useful source of the persistent nitroxyl radical anion, nitrosodisulfonate, $ON(SO_3^-)_2$ (NDS), a versatile reagent for organic conversions [1] and a common reagent for determining the kinetics and mechanisms of inorganic reactions [2–7]. The present work deals with the mechanism for the near quantitatively base-catalyzed oxidation of benzyl alcohol to benzaldehyde by NDS.

NDS is an aprotic oxidant. Prominent base-catalysis in its reactions generally arises from the formation of the conjugate base of the reducing agents, if they are sufficiently acidic, as with ascorbic acid [8] and the hydrazinium ion [9]. But alkanols are too weak an acid (pK > 15) [10,11] to form any significant amount of alkoxide to account for the $[H^+]^{-1}$ term seen in the rate. In this study, we have traced the source of the overwhelming base-catalyzed path and found the same to be associated with a hydrogen atom transfer (HAT) mechanism.

2. Experimental

2.1. Materials

Benzyl alcohol was purified by shaking it with a solution of ${\rm Fe}^{\rm II}$. The alcohol layer was then washed with distilled water

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and fractionally distilled under reduced pressure [12]. 2-Propanol (G.R, E. Merck) was purified by refluxing with CaO (200 g/L) for several hours, followed by distillation. Acetone was removed by treatment with and distillation from 2,4-dinitrophenylhydrazine. Peroxides re-form in 2-propanol if it is stood for several days [13], hence only fresh stocks of purified 2-propanol were used for the kinetic and stoichiometric studies. 2-, 3- and 4-methoxybenzyl alcohol, 4-(trifluoromethyl)benzyl alcohol (all 98%), benzyl- α, α' -dideuterated alcohol (98 atom% D) (Aldrich) and the other reagents used were of high purity and were used without further purification. Solutions were prepared from freshly boiled doubly distilled water, purged with argon.

The potassium nitrosodisulfonate dimer (Fremy's salt) in aqueous solutions undergoes nearly complete homolysis to produce the monomer, nitrosodisulfonate radical anion, \cdot NO(SO₃)₂²⁻, NDS [14]. Solid Fremy's salt was prepared and stored below 5 °C in an ammonia environment [15]. Its purity was checked by determining its oxidizing power from time to time by iodimetry and by comparing its molar absorbance at 545 nm with the literature value (20.8) [16]. Fresh preparations were thus found to be sufficiently pure. Nevertheless, on storage, the solid slowly lost its ε value, and fresh samples were prepared regularly. In the stoichiometric studies, we used preparations with an ε value of at least 19.5 M⁻¹ cm⁻¹ (at 545 nm). Potassium hydroxylamine disulfonate (HNDS) was prepared as reported [17].





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2.2. Stoichiometry and reaction products

The stoichiometry of the reaction with excess NDS in sodium hydroxide (0.40 M) under an argon atmosphere was determined by measuring the residual [NDS] spectrophotometrically.

To determine the stoichiometry under the kinetic conditions, the product mixture of NDS with excess PhCH₂OH was extracted with dichloromethane and the extract thus obtained was subjected to NMR and GC studies. Acetone produced in the reactions with 2-propanol was spectrophotometrically quantified [18].

2.3. Physical measurements and kinetics

Kinetics and absorbances were determined with a Shimadzu (UV1601) spectrophotometer, NMR spectra with a BRUKER, DPX-300 spectrometer and gas chromatograms were recorded with an Agilent, 5890N gas chromatograph. Kinetics were monitored in situ at 25.0 (± 0.2) °C, following the decrease in absorbance of NDS with time at 545 nm, where only NDS absorbs. First-order conditions were maintained using a large excess of [alcohol] over [NDS] in the NaOH media. The ionic strength was maintained at 1.0 M with NaCl. The absorbances (A_t) versus time (t) data were analyzed using non-linear least-squares regression routines to extract the rate constants. Some reactions were conducted under second-order conditions with respect to [NDS]. For such reactions the $(A_t)^{-1}$ versus time (t) data were straight lines and were used to extract the second-order rate constants. For example, reactions with substituted benzyl alcohols, [RBzOH], were carried out in 4% (v/v) acetonitrile-H₂O media under second-order conditions, [NDS] = [RBzOH]. We employed such second-order conditions because substituted benzyl alcohols have very poor solubility in water. For comparison, a few reactions of benzyl alcohol were also carried out in this medium under comparable conditions.

3. Results and discussion

3.1. Stoichiometry and reaction products

With excess NDS, spectrophotometric determination of the residual [NDS] indicated a 1:2 stoichiometry (Δ [alkanol]: Δ [NDS]) under an argon atmosphere. A similar stoichiometry was also noted under kinetic conditions with excess benzyl alcohol. For such stoichiometric determinations, the ratio of peak areas in the gas chromatogram occupied by the residual benzyl alcohol to that by benzaldehyde present in the dichloromethane-extracted product mixture was measured and found to be 17.7 (Fig. S1). Assuming complete consumption of NDS and a consumption ratio, Δ [benzyl alcohol]: Δ [NDS] of 1:2, one expects the ratio to be 19.0. GC experiments thus established a near quantitative (95.3%) conversion of benzyl alcohol to benzaldehyde.

The ratio of the integrated peak area for the benzylic hydroxyl proton to that of the –CHO proton in the NMR spectrum of the product was found to be 1.00/0.057 = 17.86 (Fig. S2). The ratio expected for a 1:2 stoichiometry is 19.00. The ratio (17.86) found therefore indicates a 94% yield.

Passage of oxygen gas retarded the reaction and decreased the yield of benzaldehyde. A plausible reason shall be discussed later.

The acetone produced in the reaction of excess 2-propanol with NDS also indicated a 1:2 stoichiometry. Therefore, the reaction of alkanols with NDS may be presented by Eqs. (1) and (2).

$$\begin{array}{c} PhCH_2OH+2(\cdot ON(SO_3)_2^{2-})\rightarrow PhCHO+2HON(SO_3)_2^{2-}\\ NDS & HNDS \end{array} \tag{1}$$

$$\begin{array}{c} \text{CH}_3\text{CHOHCH}_3 + 2(\text{`ON}(\text{SO}_3)_2^{2-}) \rightarrow \text{CH}_3\text{COCH}_3 + 2\text{HON}(\text{SO}_3)_2^{2-} \\ \text{NDS} & \text{HNDS} \end{array} \tag{2}$$

3.2. Kinetics

In alkali (>0.10 M), NDS suffers negligible bleaching [19] within 12 h. It, however, reacts rather fast with alkanols in alkali and the decay kinetics closely adhere to first-order in [NDS], [NaOH] (Fig. 1) and in [alcohol] (Fig. 2 and Table 1).

The primary alkanol, benzyl alcohol, is oxidized at a rate much faster than that for the secondary alkanol, 2-propanol. It might be noted here that the initial absorbance noted for benzyl alcohol oxidation is somewhat lower (Fig. 1a) than that for the slow reacting 2-propanol (Fig. 1b). Nevertheless, the initial absorbances for the benzyl alcohol oxidation may be extrapolated back with known rate constants and the time lapsed between mixing and recording of the first point.

3.3. Product inhibition

Kinetic order in [NDS] shifted from first-order to second-order with progressive addition of one of the reaction products, [HNDS].



Fig. 1. First-order decay in absorbance of NDS. [NDS] = 0.01 M; $T = 25.0 \degree$ C; I = 1.0 M. The solid line is the least-squares fit of absorbance – time data (black points) to first-order decay. (a) [BzOH] = 0.06 M, [NaOH] = 0.40 M (b) [2-propanol] = 0.08 M, [NaOH] = 1.0 M.



Fig. 2. Effect of reagent variations: [NDS] = 0.01 M, *I* = 1.0 M, *T* = 25.0 °C. Experimental first-order rate constants are shown in black squares, triangles or in circles where the solid lines represent linear least-squares fit: (a) [alcohol] variation; [NaOH] = 0.40 M for [BzOH], 1.0 M for [2-propanol]. 10³ slope = $(22 \pm 0.2) M^{-1} s^{-1}$ for benzyl alcohol and $(0.6 \pm 0.01) M^{-1} s^{-1}$ for [2-propanol]; (b) [NaOH] variation; [2-propanol] = 1.0 M, [BzOH] = 0.10 M.

Table 1

Representative first-order rate constants^a for the oxidation of alcohols by NDS in aqueous alkaline media. [NDS] = 0.010 M, $T = 25.0 \degree \text{C}$, I = 1.0 M.

	[NaOH] (M)	$10^3 k_{\rm o} ({\rm s}^{-1})$
[BzOH] (M)		
0.10	0.10	0.5
0.10	0.20	1.0
0.10	0.30	1.4
0.10	0.40	2.2 ^b
0.10	0.50	2.5
0.04	0.40	0.9
0.06	0.40	1.3
0.08	0.40	2.0
[2-Propanol] (M)		
1.0	0.50	0.3
1.0	0.60	0.4
1.0	0.70	0.5
1.0	0.80	0.5
1.0	1.0	0.6
0.6	1.0	0.4
0.8	1.0	0.5
0.9	1.0	0.6
1.1	1.0	0.7

^a Average of at least four parallel experiments. Individual runs reproducible within 2–4%. The regression coefficient is higher than 0.99 for an individual least-squares fit to the first-order equation.

^b $10^3 k_0 (s^{-1}) = 0.19$ for C₆H₅CD₂OH.

With sufficient excess of HNDS, the second-order plots of $(A_t)^{-1}$ versus *t* plots turned into good straight lines (Fig. S3), whereas $A_t - t$ data gave an excellent fit to first-order exponential decay in the absence of HNDS.

3.4. Primary deuterium kinetic isotope effect

Benzyl- α , α' -dideuterated alcohol (C₆H₅CD₂OH) reduced NDS with a large value ($k_{\rm H}/k_{\rm D}$ = 11.6, (Table 1)) for the kinetic isotope effect. A rate determining hydrogen atom abstraction is thus indicated.

3.5. Reactivities of substituted benzyl alcohols

Substitution at different positions of the benzyl group by different groups changed the reaction rate significantly. Compared to the unsubstituted benzyl alcohol, groups withdrawing electron density from the O–H bond accelerated the rate (Table 2). On the other hand, groups donating electron density to the O–H bond, and thus strengthening the bond, retarded the reaction rate. These observations support an α -C–H bond breaking at the rate determining step.

3.6. Origin of the $[OH^{-}]$ dependence on rate

Alkanols themselves are too weak an acid to undergo kinetically significant deprotonation. However, formation of an N-bound precursor of alkanol with NDS may assist deprotonation of the alkanol. Similar precursors of NDS with water and hydroperoxide have been reported earlier [2,6,20]. When rapid equilibrium formation of the N-bound precursor is incorporated (Eq. (7)) in the reaction scheme (Scheme 1) framed with benzyl alcohol as the paradigm, the base-catalysis is accounted for.

A steady state assumption for the PhCHO⁻ radical leads to the rate law Eq. (7).

$$Rate = k_1 k_2 K[NDS]^2 [BzOH] / \{k_{-1}[HNDS] + k_2 [NDS]\} [H^+]$$
(7)

Under the condition, k_2 [NDS] $\gg k_{-1}$ [HNDS], Eq. (7) is reduced to Eq. (8) and the reactions follow a first-order kinetics in [NDS] when [HNDS] is relatively small.

$$Rate = k_1 K[NDS][BzOH]/[H^+]$$
(8)

The experiments well verified this rate law (Fig. S3).

Further, under the conditions k_{-1} [HNDS] $\gg k_2$ [NDS], the rate equation reduces to Eq. (9) and a second-order kinetics is observed at a sufficiently high [HNDS].

Table 2

Second-order rate constants^a (k'_2) for the oxidation of substituted benzyl alcohols. [NDS] = 0.01 M, [alcohol] = 0.01 (M), [NaOH] = 1.0 M, $T = 25.0 \degree$ C, I = 1.0 M, 4% (v/v) CH₃CN-H₂O media.

Substitution	$k'_2 \ (\mathrm{M}^{-1} \ \mathrm{s}^{-1})$
4-(Trifluoro methyl) 3-Methoxy Benzyl alcohol ^c 4-Methoxy 2-Methoxy	$\begin{array}{c} 0.26^{b} \\ 0.12^{b} \\ 0.03 \\ 0.02^{d} \\ 0.01^{d} \end{array}$

^a Average of at least four parallel experiments. Individual runs reproducible within 2–4%. The regression coefficient is higher than 0.99 for individual absorbance (A_t) versus time (t) least-squares fit to the first-order equation.

^b Groups withdrawing electron density from the O–H bond accelerate the rate in comparison to benzyl alcohol.

^c Experiments conducted under the same conditions as for others.

^d Groups donating electron density towards the O-H bond, and thus strengthening the bond, accelerate the rate in comparison to benzyl alcohol.



Scheme 1. Proposed mechanism for the oxidation of benzyl alcohol by NDS.

$$Rate = k_1 k_2 K[NDS]^2 [BzOH] / \{k_{-1}[HNDS]\} [H^+]$$
(9)

Fig. S3 illustrates how progressive addition of HNDS changes the kinetics from first-order to second-order in [NDS] and $(A_t)^{-1}$ versus time plots exhibit good linearity in the presence of 0.15 M HNDS. Moreover, Fig. S3 also includes an excellent non-linear fit $(r^2 = 0.999)$ of absorption *versus* time data confirming the secondorder decay of [NDS] at high [HNDS].

3.7. Effect of oxygen

NDS does not catalyze the auto-oxidation of benzyl alcohol. Dissolved oxygen prolongs reaction time and lowers the yield of benzaldehyde. Possibly, dissolved oxygen consumes PhCOH.⁻ and thus the reaction goes astray.



Fig. 3. Effect of dissolved oxygen on the kinetics: [2-propanol] = 1.0 M, [NDS] = 0.01 M, [NaOH] = 0.50 M, T = 25.0 °C, I = 1.0 M, (A): ambient atmosphere, (B): argon-saturated media.

Further, the standard potential for the conversion HNDS \rightarrow NDS is high (E° versus NHE in water is 1.36 V) [21]. This may be an additional barrier to the operation of an NDS/HNDS catalytic cycle.

In the presence of dissolved oxygen the reaction course changes (Fig. 3). So, we determined the kinetics under an argon atmosphere to minimize the effect of dissolved oxygen on the reaction rate.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.01.018.

References

- [1] H. Zimmer, D.C. Lankin, S.W. Horgan, Chem. Rev. 71 (1971) 229.
- E.S. Gould, Acc. Chem. Res. 18 (1985) 22.
- S.K. Ghosh, E.S. Gould, Inorg. Chem. 28 (1989) 3651. [3]
- S.K. Saha, M.C. Ghosh, E.S. Gould, Inorg. Chem. 31 (1992) 5439.
- [5] S.P. Ghosh, M.C. Ghosh, E.S. Gould, Int. J. Chem. Kinet. 26 (1994) 665.
- P.N. Balasubramanian, E.S. Gould, Inorg. Chem. 22 (1983) 1100.
- Z. Yang, E.S. Gould, J. Chem. Soc., Dalton Trans. (2002) 3840.
- Z. Yang, E.S. Gould, Res. Chem. Intermed. 29 (2003) 181.
- G. Gualtieri, S. Colacicchi, C. Corvaja, J. Chem. Soc., Perkin Trans. 2 (2002) 1917.
- [10] F.M. Menger, M. Ladika, J. Am. Chem. Soc. 109 (1987) 3145.
- [11] See also G.O. Andrés, R.H. de Rossi, ARKIVOC X (2003) 127.
- [12] J.H. Mathews, J. Am. Chem. Soc. 48 (1926) 562.
- [13] L.E. Gilson, J. Am. Chem. Soc. 54 (1932) 1445.
- [14] (a) R.W. Z Asmussen, Anorg. Allg. Chem. 212 (1933) 317; (b) B.J. Wilson, J.M. Hayes, J.A. Durbin, Inorg. Chem. 15 (1976) 1703.
- [15] S. Yamada, R. Tsuchida, Bull. Chem. Soc. Jpn. 32 (1959) 721.

- [16] J.H. Murib, D.M. Ritter, J. Am. Chem. Soc. 74 (1952) 3394.
 [17] G.K. Rollefsoann, C.F. Oldershaw, J. Am. Chem. Soc. 54 (1932) 977.
 [18] Vogel's Textbook of Quantitative Chemical Analysis, fifth Ed., Longmans Scientific and Technical, New York, 1989, p. 706.
- [19] B.J. Wilson, D.L. Fillmore, Inorg. Chem. 16 (1977) 1404.
 [20] B.J. Wilson, D.M. Ritter, Inorg. Chem. 2 (1963) 974.
 [21] V.F. Toropova, V.N. Degtyareva, Izv. Vyssh. Uchebn. Zaved. 17 (1974) 175 (Chem. Abs. 80 (1974) 152439q).