Mo(VI)-catalysis of perborate oxidation of aryl sulfides in acetic acid

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Molybdenum(VI) catalyses effectively the sodium perborate oxidation of aryl sulfides to sulfoxides in glacial acetic acid. The catalysed oxidations of diphenyl sulfide and S-phenylmercaptoacetic acids are zero order with respect to the oxidant and first order with respect to the sulfides and Mo(VI). Trichloroacetic acid enhances the oxidation. Glacial acetic acid is a suitable solvent; methanol or ethylene glycol suppresses the reaction. The kinetic results reveal dioxoperoxomolybdenum(VI) as the reactive oxidant.

Keywords: perborate, sulfides, molybdenum(VI), catalysis, oxidation

Economic and environmental constraints necessitate replacement of oxidation procedures requiring large amounts of heavy metals by catalytic alternatives using clean oxidants. Particularly of interest are procedures that use readily available catalysts and cheap oxygen sources. Sodium perborate ($NaBO_3.4H_2O$), a peroxo salt of anionic formula $[B_2(O_2)_2(OH)_4]^{2-}$, is an inexpensive, innocuous, easily handled, stable, large-scale industrial chemical primarily used in detergents. It is an effective reagent in organic synthesis, acetic acid is the solvent of choice[1-3] and we reported recently the mechanisms of oxidation of organic sulfides and anilines in glacial acetic acid.[4,5] In aqueous acetic acid perborate behaves as H_2O_2 and metal ion catalysis is that of H_2O_2 oxidation;[6,7] presence of water reduces the efficiency and is of little synthetic utility.[1] So far there is no report on metal ion-catalysed perborate oxidation in glacial acetic acid, hence this work. Muzart[8] reports Cr(VI)-assistance of perborate oxidation in benzene–water (1:1) under phase transfer conditions.

Results and discussion

Sodium perborate (SPB) is insoluble in organic solvents like methanol, ethanol, 2-propanol, *t*-butanol, dimethylformamide, dioxane, acetonitrile, 2-ethoxyethanol, 2-butoxyethanol, 2-methoxypentan-2,3-diol and glycerol but readily dissolves in acetic acid and less so in ethylene glycol. In acetic acid, with catalytic amount of Na_2MoO_4, SPB effectively oxidises diphenyl sulfide to diphenyl sulfoxide, identified by its IR spectrum (1034 cm^{-1}) and melting point (69 °C; lit. 70 °C); the yield is 75%. S-Phenylmercaptoacetic acid is oxidised to phenylsulfinylacetic acid, identified by its IR spectrum; 1078 (SO), 1724 (C = O), 3423, 3227, 3023 (OH) cm^{-1}. While Mn(II), Fe(II), Ni(II), Cu(II), Cd(II), Hg(II), Sn(II), Pb(II) and Bi(III) do not catalyse the oxidation and Cr(VI), Co(II) and Pd(II) catalyse the decomposition of the oxidant. $Mn(OCOCH_3)_2.4H_2O$, $Fe(OCOH)_2.2H_2O$, $NiCl_2.6H_2O$, $Cu(OCOCH_3)_2.H_2O$, $Cd(OCOCH_3)_2.2H_2O$, $Hg(OCOCH_3)_2$, $SnCl_2.2H_2O$, $Pb(OCOCH_3)_2.3H_2O$, $Bi(NO_3)_3.5H_2O$, $K_2Cr_2O_7$, $Co(NO_3)_2.6H_2O$ and $Pd(OCOCH_3)_2$ were the salts used. Many salts of transition and inner transition metals available in the market ($K_2TiO(C_2O_4)_2.2H_2O$, $[NH_4]VO_3$, $(NH_4)_6Mo_7O_{24}.4H_2O$, Li_2MoO_4, $Na_2WO_4.2H_2O$, $FeSO_4.7H_2O$, $Fe(NH_4)_2(SO_4)_2.6H_2O$, $Fe(NH_4)(SO_4)_2.12H_2O$, $Ce(SO_4)_2.4H_2O$, $Ce(NH_4)_4(SO_4)_4.2H_2O$ and $Ce_2(C_2O_4)_3.9H_2O$) are insoluble in glacial acetic acid and could not be employed as catalysts. Oxoacids of transition metals (vanadic, molybdic and tungstic acids) and phosphomolybdic and phosphotungstic acids also do not dissolve in glacial acetic acid. Although Zr(IV) catalyses the oxidation the catalytic efficiency is only about one-half of Mo(VI) and the kinetic results lack reproducibility; $ZrOCl_2.8H_2O$ was the salt used.

The kinetics of Mo(VI)-catalysed perborate oxidations of diphenyl sulfide (DPS) and S-phenylmercaptoacetic acid (PMA) in glacial acetic acid were studied under the condition: [sulfide] > [SPB] >> [Mo(VI)] by iodometric estimation of the unconsumed oxidant at different reaction times. The catalysed oxidations of aliphatic sulfides are too fast to follow by titrimetry. The reactions are zero order with respect to the oxidising agent and first order with respect to the sulfides; the concentration of the unreacted substrate decreases exponentially with reaction time and the least-squares fit yields the pseudo-first order rate constant, k' = rate/[sulfide] (Fig. 1); the concentration of unreacted sulfide was deduced from the experimentally determined concentration of the oxidant; $[\text{sulfide}] = \{[\text{sulfide}]_0 - ([\text{oxidant}]_0 - [\text{oxidant}])\}$. Also, the pseudo-first order rate constants do not differ significantly on varying the initial concentration of perborate or sulfide (Table 1). The reaction is first order with respect to Mo(VI), as seen from the linear plots of k' versus [Mo(VI)] through the origin (Fig. 2). The uncatalysed reactions are clean second-order; first order each with respect to the oxidant and substrate, and are slow. For example, the second-order rate constant of oxidation of DPS at 35 °C is 8.8×10^{-3} M^{-1} s^{-1}. Trichloroacetic acid (TCA) facilitates the Mo(VI)-catalysed perborate oxidation, the Mo(VI)-catalysed oxidation rate increases linearly with [TCA] (Fig. 3). Acetic acid is the most suitable solvent for the title study; the oxidation rate of DPS in ethylene glycol, under identical concentrations, is only about 2 % of that in glacial acetic acid. Also, addition of ethylene glycol (EG) or methanol to the reaction solutions

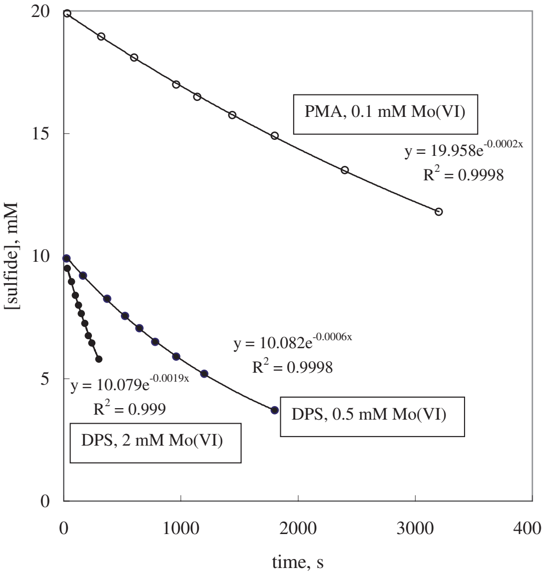

Fig. 1 Mo(VI)-catalysed SPB oxidation in acetic acid. First order in sulfides. $[SPB]_0$ = 5–12 mM, temp. 35 °C.

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Table 1 Pseudo-first order rate constants for Mo(VI)-catalysed SPB oxidation of organic sulfides in acetic acid

$[\text{Sulfide}]_0$, mM	10^4 k', s^{-1}	
	DPS[a]	PMA[b]
10	4.8, 4.6[c]	1.7
15	4.8	1.6
20	4.8	1.7, 1.7 [d], 1.6 [e]
25	4.8	1.6
30	4.6	

$[\text{SPB}]_0$ = 5 mM, temp. 35 °C; [a]$[\text{Mo(VI)}]_0$ = 0.5 mM; [b]$[\text{Mo(VI)}]_0$ = 0.1 mM; [c]$[\text{SPB}]_0$ = 3 mM; [d]$[\text{SPB}]_0$ = 8 mM; [e]$[\text{SPB}]_0$ = 12 mM.

suppresses the oxidations (Table 2). Further, dissolution of SPB in acetic acid or ethylene glycol makes little difference in the kinetic results. Boric acid and borate do not influence the oxidation (Table 3). The oxidations do not occur *via* a radical mechanism; addition of vinyl monomer, acrylamide to the reaction solutions neither leads to polymerisation nor arrests the oxidations. The measured oxidation rates at 20, 35 and 50 °C afford the activation parameters.

The effect of substituents on the oxidation was examined by measuring the reaction rates of six *para*-substitued S-phenylmercaptoacetic acids. In each case, the reaction is first order in the substrate and zero order in the oxidant; the concentration of the unreacted substrate decreases exponentially with reaction time. Table 4 lists the second order rate constants ($k_2 = k'/[\text{Mo(VI)}]$) at 20–50 °C and the thermodynamic parameters, calculated using the Eyring equation. The Mo(VI)-catalysed SPB oxidation of S-phenylmercaptoacetic acids and diphenyl sulfide conforms to the isokinetic relationship; the double logarithmic plot of k_2(50 °C) versus k_2(20 °C) is a straight line (R^2 = 0.97, SD = 0.03).

Table 2 Influence of solvents on Mo(VI)-catalysed SPB oxidation of diphenyl sulfide

% (v/v)			10^4 k', s^{-1}
HOAc	MeOH	EG	
100	0	0	4.8
80	20	0	3.4
70	30	0	2.3
60	40	0	1.6
80	0	20	1.2
80	0	20[a]	1.3
0	0	100	0.09

$[\text{SPB}]_0$ = 5 mM, $[\text{DPS}]_0$ = 10mM, $[\text{Mo(VI)}]_0$ = 0.5 mM, temp. 35 °C; [a]SPB dissolved in EG.

Table 3 Lack of influence of borate and boric acid on Mo(VI)-catalysed SPB oxidation of diphenyl sulfide in acetic acid

$[\text{SPB}]_0$, mM	$[\text{NaBO}_2]_0$, mM	$[\text{H}_3\text{BO}_3]_0$, mM	10^4 k', s^{-1}
5	0	0	4.8
5	10	0	4.8
5	0	10	4.9

$[\text{DPS}]_0$ = 10 mM, [Mo(VI)] = 0.5 mM, temp. 35 °C.

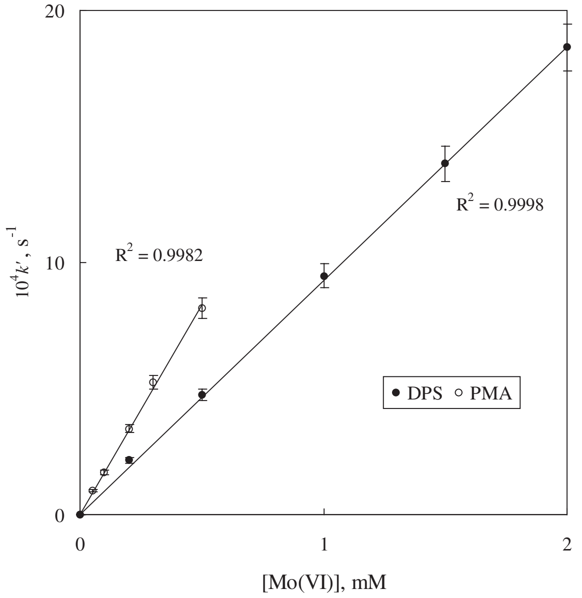


Fig. 2 Mo(VI)-catalysed SPB oxidation in acetic acid. First order in Mo(VI). $[\text{SPB}]_0$ = 5 mM, $[\text{sulfide}]_0$ = 10 mM, temp.35 °C.

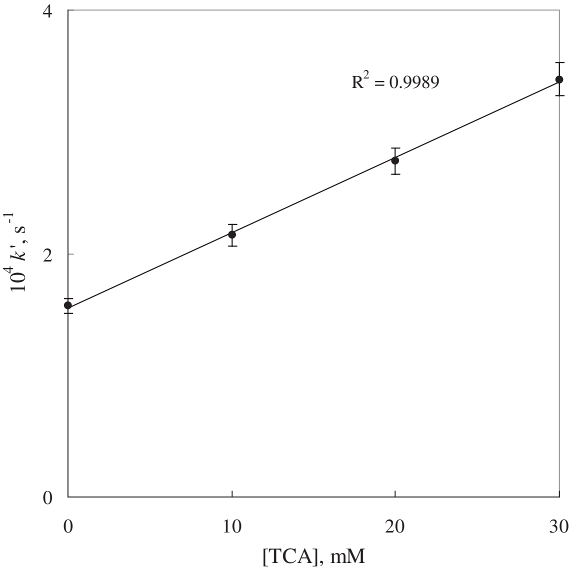


Fig. 3 Mo(VI)-catalysed SPB oxidation in acetic acid. Acid catalysis. $[\text{SPB}]_0$ = 5 mM, $[\text{DPS}]_0$ = 10 mM, [Mo(VI)] = 0.5 mM, temp. 35 °C.

The existence of the Exner relationship reveals that all the sulfides are oxidised by a common mechanism. Analysis of the structure-reactivity relationship shows that the oxidation of S-phenylmercaptoacetic acids conforms to the Hammett equation at all the temperatures studied (R^2 = 0.99, SD = 0.02–0.01). The negative ρ-values –0.54, –0.48, and –0.46 at

Table 4 Second-order rate constants for Mo(VI)-catalysed SPB oxidation in acetic acid

Substrate	k_2, M^{-1} s^{-1}			ΔH#, kJ mol^{-1}	ΔS#, J K^{-1} mol^{-1}
	20	35	50 °C		
$C_6H_5SC_6H_5$	0.27	0.95	2.7	57.5	–59
$C_6H_5SCH_2COOH$	0.71	1.7	4.7	47.0	–88
p-$CH_3C_6H_4SCH_2COOH$	0.79	2.1	5.8	49.7	–77
p-$CH_3OC_6H_4SCH_2COOH$	0.90	2.3	6.5	49.4	–77
p-$ClC_6H_4SCH_2COOH$	0.47	1.4	3.8	52.5	–72
p-$BrC_6H_4SCH_2COOH$	0.46	1.4	3.9	53.2	–70
p-$NO_2C_6H_4SCH_2COOH$	0.25	0.72	2.1	52.8	–76

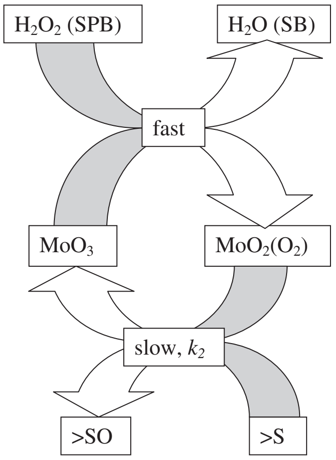
20, 35, and 50 °C, respectively) point to an electron-deficient sulfur atom in the transition state. Further, the reaction constant (ρ) compares with those of (i) Mo(VI)-catalysed oxidation in aqueous acetic acid which is zero, first and second order in SPB, PMA and Mo(VI), respectively,[9] (ii) W(VI)-catalysed oxidation in aqueous acetic acid which is first order in SPB and exhibits Michaelis-Menten kinetics with respect to PMA and W(VI)[6] and (iii) uncatalysed second-order oxidation in glacial acetic acid[4] and in acetic acid–ethylene glycol with SPB dissolved in ethylene glycol (excluding *p*-nitro-S-phenylmercaptoacetic acid which follows different kinetics)[10] (–0.98 at 45 °C, –0.55 at 55 °C, –0.83 to –0.77 at 45–65 °C and –0.80 to –0.72 at 50–60 °C, respectively).

SPB on dissolution in glacial acetic acid yields equivalent amount of H_2O_2, and on aging peracetic acid is generated at the expense of H_2O_2.[4,5,11] In acetic acid, Na_2MoO_4 exists as MoO_3, the coordinated water molecule omitted.[12] With H_2O_2, MoO_3 forms two peroxo species, dioxoperoxomolybdenum (VI) [$MoO_2(O_2)$] and oxodiperoxomolybdenum(VI) [$MoO(O_2)_2$], one of which is the reactive oxidant.[12-15] The non-dependence of the reaction rates on [oxidant] reveals rapid formation of the reactive peroxo species of Mo(VI). Since the reaction is first order in Mo(VI) and the sulfides, the oxidation of the sulfides by the reactive peroxo-molybdenum(VI) species is slow and rate determining. The ambiguity in the oxidising peroxo-molybdenum(VI) species is sorted out by conducting kinetic experiments breaching the condition: [Mo(VI)] << $[\text{oxidant}]_0$. If oxodiperoxomolybdenum(VI) were to be the reactive oxidant, under the condition: [sulfide] >> $[\text{SPB}]_0 \approx 2.5$ [Mo(VI)], the reaction should follow first-order kinetics with respect to the oxidant which is contrary to the experimental findings (Fig. 1); beyond 20 % completion of the oxidation [$MoO(O_2)_2$] should deplete due to lack of oxygen source to regenerate. On the other hand, dioxoperoxomolybdenum(VI) as the oxidising species, under the same experimental conditions, demands the oxidation to be zero order with respect to the oxidant which is an experimental fact; [$MoO_2(O_2)$] is regenerated up to 60 % completion of the oxidation, rendering the reaction zero order with respect to the oxygen source. Scheme 1 presents the mechanism of the catalysed oxidation with dioxoperoxomolybdenum(VI) as the reactive oxidising species. A possible explanation for the enhancement of Mo(VI)-catalysed oxidation rate by trichloroacetic acid is that [$MoO_2(O_2)$] is susceptible to protonation and the protonated species is a better oxidant than the unprotonated one. Although SPB generates peracetic acid on aging in acetic acid [4,5,11] the possibility of Mo(VI)-catalysed formation of peracetic acid and the oxidation turning to be peracetic acid oxidation is unlikely; the peracetic acid oxidation of DPS and PMA, under identical conditions, are almost instantaneous.[4]

Experimental

Sodium perborate (SPB) was used as received. Diphenyl, diethyl and di-*n*-butyl sulfides (Fluka) were redistilled before use. S-Phenylmercaptoacetic acids were prepared using standard methods and recrystallised. Acetic acid was refluxed over CrO_3 for 6 h and distilled through a column. All the chemicals used were of AR or LR grade.

SPB (10 mmol) was added to diphenyl sulfide (10 mmol) and Na_2MoO_4 (1 mmol) in acetic acid (10 ml) at 50 °C, the solvent was evaporated after 1 h and the product extracted with ether and dried over anhydrous Na_2SO_4.



$k_2 = k'$[Mo(VI)] ; $k' =$ rate/[>S]

Scheme 1

Fresh solutions of SPB as well as Na_2MoO_4 in acetic acid were used for the kinetic study. Aging of SPB solution in acetic acid generates peracetic acid[4,5,11] while the catalyst is precipitated from Na_2MoO_4 solution in acetic acid on standing. The reactions were initiated by the addition of sulfides in acetic acid to SPB and Na_2MoO_4 in acetic acid. The progresses of the oxidation at constant temperature, under the condition: [sulfide] > [SPB] >> [Mo(VI)], was followed up to 80 % consumption of the oxidant by iodometric estimation of the same.

Conclusions

Study of SPB oxidation in glacial acetic acid with a variety of metal salts reveals Na_2MoO_4 as the effective catalyst; the oxidation of PhSPh yields PhSOPh in good yield. The reactive oxidant, inferred from the kinetic results, is dioxoperoxomolybdenum(VI).

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