JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. **12**, 758–764 (1999)

Reduction of *o*-iodosobenzoate ion by sulfides and its oxidative regeneration

Clifford A Bunton,* Houshang J Foroudian and Nicholas D Gillitt

Department of Chemistry, University of California, Santa Barbara, California, 93106, USA

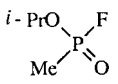
Received 24 May 1999; revised 13 July 1999; accepted 16 July 1999

ABSTRACT: *o*-Iodosobenzoate and *o*-iodoxybenzoate ion (IBA and IBX, respectively) are turnover catalysts of hydrolyses of phosphonofluoridates and non-toxic simulants. Reactions of IBA with phosphonothioates are stoichiometric because sulfides (e.g. 4-methoxybenzenethiol) reduce IBA to *o*-iodobenzoate ion. Oxidants, e.g. HSO_5^-, as OXONE, and magnesium peroxyphthalate, MPPA, regenerate IBA and gradually oxidize it to IBX, which eventually decomposes. The procedure was tested on hydrolyses of *p*-nitrophenyl diphenylphosphate (*p*NPDPP) and 4-nitrobenzenesulfonyl fluoride, 1, catalyzed by IBA, and the catalyzed hydrolysis of 1 was examined. Some of the oxidation products of 4-methoxybenzene thiol were identified by ^{1}H NMR spectroscopy and oxidative decomposition of IBX was monitored. Periodate ion slowly oxidized *o*-iodobenzoate ion to IBA and IBX. Copyright © 1999 John Wiley & Sons, Ltd.

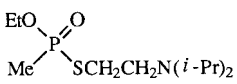
KEYWORDS: *o*-iodosobenzoate; *o*-iodoxybenzoate; sulfonyl fluorides; dephosphorylation; peroxymonosulfate; peroxyphthalate; hydrolysis

INTRODUCTION

Nerve agents, both phosphonofluoridates, e.g. GB (Sarin) and phosphonothioates, e.g. VX, react readily with



GB



VX

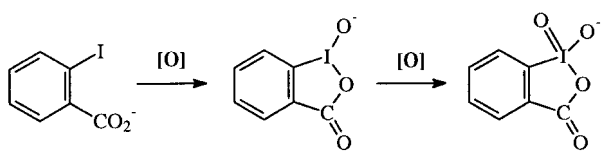
nucleophiles.[1] *o*-Iodoso- and *o*-iodoxybenzoate, IBA and IBX respectively, are effective nucleophiles towards toxic phosphonofluoridates and nontoxic model compounds, e.g. triarylphosphates.[2,3] The reactions of IBA and IBX are catalytic, whereas many nucleophiles react stoichiometrically. However, the reaction of IBA with phosphonothioate simulants of VX is not catalytic because IBA is reduced by thiols and their derivatives.[4]

The chlorosulfide blister agents, e.g. HD and Mustard Gas, do not react bimolecularly with nucleophiles or bases except in forcing conditions, but, like VX, they are readily decontaminated by oxidation.[1] A few compounds

$$(ClCH_2CH_2)_2S$$

HD

react as nucleophiles and oxidants, e.g. hypochlorite ion and N-chloroamines,[1] but they are aggressive reagents. Peroxy acids, e.g. HSO_5^-, are good oxidants at sulfur,[5] and peroxycarboxylate ions are effective nucleophiles towards phosphoryl centers,[6] but these reactions occur at different pH values. The combination of a turnover nucleophile, e.g. IBA, and a peroxy acid may therefore provide a system which oxidizes at sulfur, and reacts nucleophilically at phosphorus. The requirements are that the oxidant be effective towards sulfur compounds and capable of re-oxidizing *o*-iodobenzoate ion, IB, to IBA and/or IBX. Peroxy acids are obvious candidates for this purpose, but periodate ion oxidizes sulfides[7] and might also oxidize IB.



IB **IBA** **IBX**

We planned to use HSO_5^-, as OXONE ($2KHSO_5$ $KHSO_4$ K_2SO_4),[5] or magnesium peroxyphthalate, MPPA, as oxidants, the latter is convenient because its peroxy anion is an effective dephosphorylating agent.[6] *p*-Nitrophenyl diphenylphosphate (*p*NPDPP) is often used as a model for the toxic fluoridates in reactions with nucleophiles, but its low solubility in aqueous media is a disadvantage. We therefore examined 4-nitrobenzenesulfonyl fluoride, **1**, as a model substrate towards IBA.

**Correspondence to:* C. A. Bunton, Department of Chemistry, University of California, Santa Barbara, CA 93106, USA. E-mail: bunton@chem.ucsb.edu

CCC 0894–3230/99/100758–07 $17.50

Table 1. ^{1}H NMR chemical shifts.[a]

IBA	8.19, d, d; 7.98, t, d; 7.89, d; 7.75, t
IB	7.87, d; 7.42, t; 7.40, d; 7.10, t, d
4-$O_2NC_6H_4SO_2F$	8.60, d; 8.37, d
4-$O_2NC_6H_4SO_3$	7.80, d; 7.08, d
4-$MeOC_6H_4SH$	7.30, d; 6.79, d
(4-$MeOC_6H_4S)_2$	7.37, d; 6.91, d
MPPA	7.68, m, 3H; 7.55, t, 1H
Phthalate ion	7.59, m; 7.47, m
C_6H_5I	7.69, d; 2H; 7.41, t, 1H; 7.17, t, 2H

[a] In H_2O–*t*-BuOH 7:3 v/v with TSP in D_2O as external reference. Vicinal coupling constants are 7–8 Hz, and long-range coupling constants, where observed, are ca. 1 Hz.

This reaction can be followed spectrophotometrically and products can be monitored by using NMR spectroscopy.[8]

Some of the results of this work were presented at the ERDEC Scientific Conference on Chemical and Biological Defense Research, November 1998,[8] where Professor Moss told one of us of his new work in this area.[9] This work materially extends understanding of reactions of IBA and IBX with thioates and their hydrolysis products in cationic micelles.[4]

RESULTS AND DISCUSSION

Hydrolysis of 4-nitrobenzenesulfonyl fluoride, 1

The IBA catalyzed hydrolysis of **1** was followed at pH 8.5 over a range of [IBA] (Fig. 1). The first-order rate constant, k_{obs}, with respect to **1** varied linearly with [IBA]. The data point with **1** in excess over IBA fit on the plot (Fig. 1), indicating that IBA is a turnover catalyst. There was a small contribution from a spontaneous hydrolysis. With [IBA] $>10^{-3}$ M we saw an induction period (<7 s) before the intermediate, **3** (Scheme 1) came into steady state.

The overall reaction (Scheme 1) is shown with a mechanism similar to that observed in dephosphorylation, where breakdown of the intermediate involves nucleophilic attack on the iodoso residue.[2,12] The second-order rate constant is 20.4 ± 0.5 M^{-1} s^{-1} at 25.0 °C (Fig. 1, $r = 0.998$). The pK_a of *o*-iodosobenzoic acid is 7.35 in water[13] and an apparent value of 7.25 was estimated from kinetics of reactions in cationic micelles.[14]

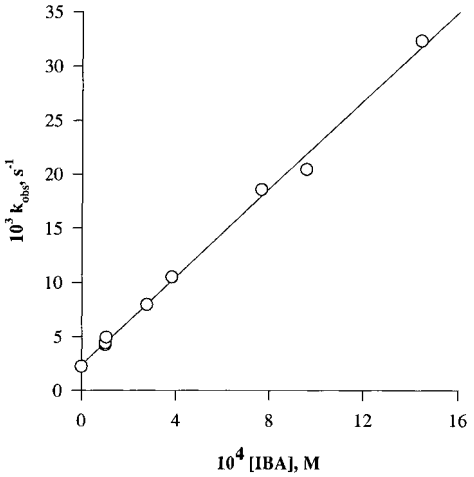
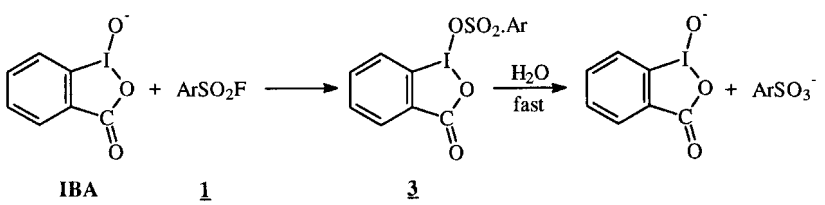


Figure 1. Hydrolysis of 4-nitrobenzenesulfonyl fluoride catalyzed by IBA in water, pH 8.5, and 25.0 °C

Reduction of IBA and its regeneration by HSO_5^-

We used ^{1}H NMR spectroscopy to monitor reduction of IBA (5×10^{-3} M) by 4-methoxybenzene thiol, **4**, and the subsequent oxidation of *o*-iodobenzoate ion, IB. Unless specified all NMR reactions were carried out in H_2O–*t*-BuOH 7:3 v/v, 0.1 M $NaHCO_3$, nominal pH = 7.5. This solvent was used to solubilize the sulfide and some of its oxidation products. We use protio solvents with signal suppression and only monitored signals in the aromatic region. There is overlap between ^{1}H NMR signals of the iodine compounds, but in order of decreasing chemical shift the multiplicities are: for IBA, d, t, d, t, and for IBX, d, d, t, t. The ^{1}H NMR signals of the sulfur compounds are all doublets, which assists identification of products and intermediates.

The ^{1}H NMR signals of IBA disappeared within the time of signal measurement (8–10 min); on addition of 5×10^{-3} M thiol, **4**, signals of IB appeared and those of **4** were replaced by signals of the disulfide, **5** (Table 1), and signals of an intermediate, **6a**, at 7.31 and 6.44 ppm, d [Fig. 2 (A)]. There was signal overlap, but signals had the expected multiplicity. We then added 0.025 M HSO_5^- and signals of IBA reappeared with signals of 4-methoxybenzenesulfonate, **7**, at 7.79 and 7.04 ppm, d. Signals of intermediate, **6a**, correspondingly decreased (Fig. 2), but those of a second intermediate, **6b**, appeared at 7.54 and



Scheme 1. Hydrolysis of 4-nitrobenzenesulfonyl fluoride catalyzed by IBA in water, pH 8.5, and 25.0 °C

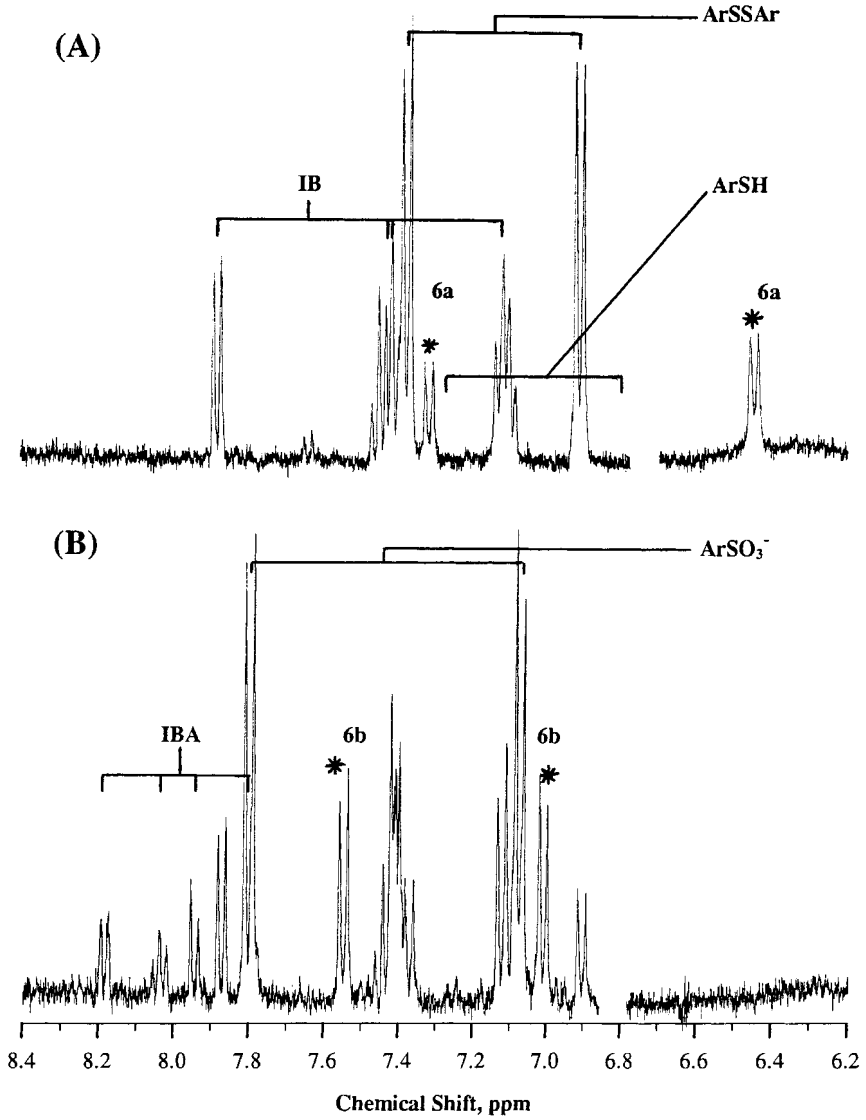


Figure 2. Reduction of IBA (5×10^{-3} M) by 4-methoxybenzene thiol (5×10^{-3} M) at 21 °C. (A) Initial reduction. (B) After addition of HSO_5^-. Chemical shifts of the identified compounds are indicated and * indicates signals of intermediates, 6a,b Ar = 4−$MeOC_6H_4$

7.01 [Fig. 2 (B)]. Within the time required for running the spectrum (ca. 10 min) we saw no signals of IBX, but IB was not completely oxidized back to IBA [Fig. 2 (B)] and there was overlap with a signal of **4**.

The spectrum changed with time and after 1 day at 21 °C signals of IBA had decreased and those of IBX appeared at 8.26, d, 8.06, t and 7.91, t, ppm, each corresponding to ^1H, although there is overlap with the signal of IBA at 8.18 ppm. The signals of the intermediate sulfur compounds, **5** and **6a,b**, disappeared and were replaced by those of the sulfonate, **7**. The signal-to-noise ratio deteriorated with respect to IBA and IBX as they gradually decomposed, but the spectrum did not change within a further 3 days, probably because HSO_5^- had been used up. We then added 0.25 M HSO_5^- and all signals of aromatic iodine compounds disappeared, but those of 4-methoxybenzenesulfonate, **7**, remained.

The oxidation of IB by HSO_5^- is illustrated by the data in Table 2 and Fig. 3 (A) with no sulfur compounds, and within 10 min of mixing. Within this time there was formation of IBA and IBX, depending on $[HSO_5^-]$, but no loss of aromatic iodo compounds. In a separate experiment with 0.01 M IB and 0.102 M HSO_5^- the IB signal disappeared within 65 min at 21 °C and there were signals

Table 2. Oxidation of IB by HSO_5^- [a]

$[HSO_5^-]$, M	$[HSO_5^-]/[IB]$	χ_{IB}	χ_{IBA}	χ_{IBX}
0.0104	0.51	0.82	0.18	—
0.0174	0.85	0.24	0.63	0.13
0.0338	1.65	—	0.78	0.22
0.0846	4.13	—	0.71	0.29

[a] In H_2O–*t*-BuOH 7:3 v/v, pH 8.6, 0.1 M $NaHCO_3$.

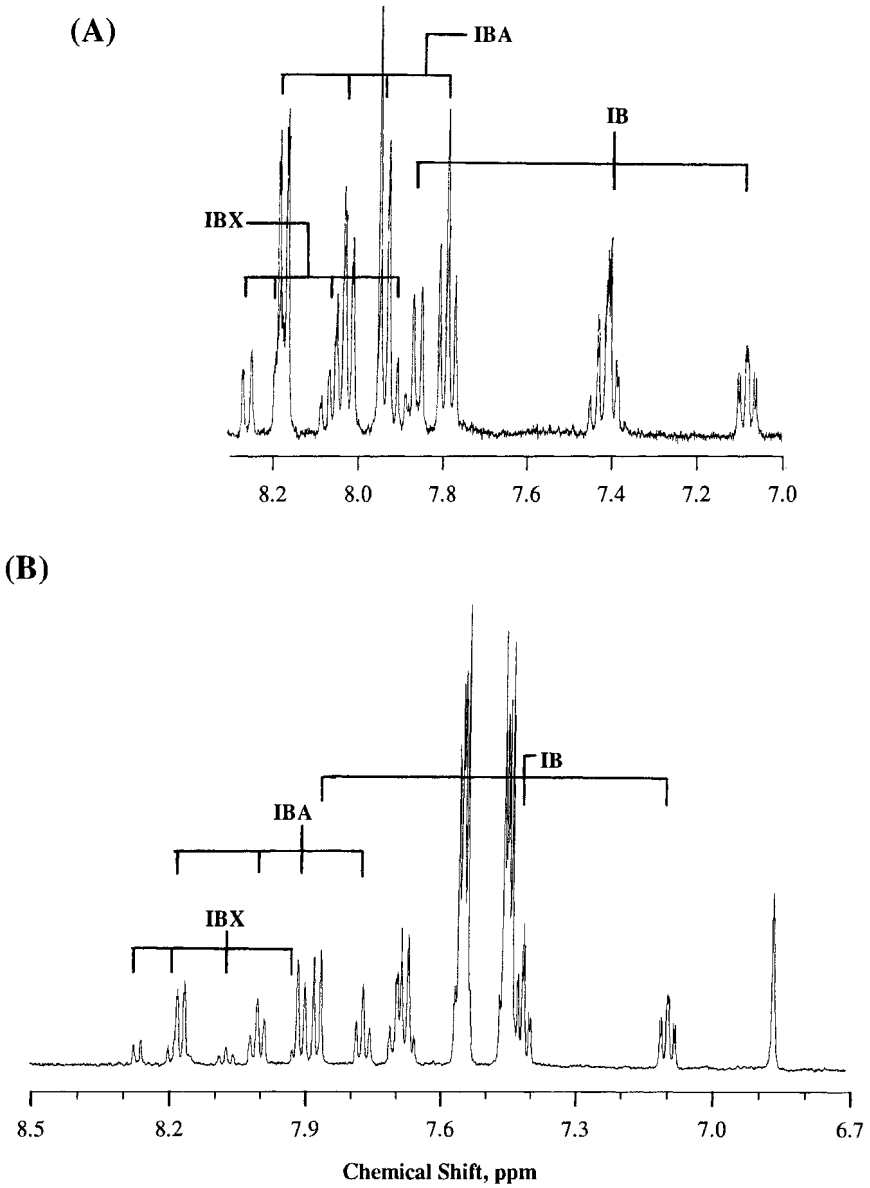


Figure 3. (A) Reaction of IB (0.021 M) with 0.017 M HSO_5^- after 20 min at 21 °C. (B) Reaction of IBA (0.02 M) with equimolar MPPA after 41 min at 21 °C

of IBA and IBX in the ratio 1:1.8. On the basis of comparison of signal areas with that of mesitoate ion the combined concentrations of IBA+IBX were 53% of the original [IB], showing that IBX was decomposing before its complete formation from IBA. Even with modest concentration of HSO_5^- (ca. 0.1 M) the decomposition of IBX (and IBA) is inconveniently rapid.

We established regeneration of IBA as a catalyst of the hydrolysis of 4-nitrobenzene sulfonyl fluoride. We reduced 0.01 M IBA with 0.01 M 4-methoxybenzene thiol, **4**, then added 0.05 M HSO_5^- followed by 0.01 M sulfonyl fluoride. Within the time required to collect the ^{19}F NMR spectrum (8–10 min), the signal of the sulfonyl fluoride had disappeared and we saw only that of F. Control experiments confirmed that the spontaneous hydrolysis is relatively slow in solutions of OXONE. Qualitative observations on the hydrolysis of pNPDPP are described in the Experimental section.

Reactions of peroxyphthalate ion

Magnesium peroxyphthalate, MPPA, behaves similarly to HSO_5^- in its reactions. When 0.01 M 4-methoxybenzene thiol, **4**, was mixed with equimolar MPPA, signals of **4** disappeared and new signals (doublets) of disulfide, **5**, appeared at 7.37 and 6.91 ppm, and those of the sulfonate, **7**, appeared at 7.80 and 7.08 ppm. We did not see signals at 7.31 and 6.44 ppm of the intermediate, **6**, which was formed in the reaction with HSO_5^- (Fig. 2),

Table 3. Oxidations by MPPA[a]

[MPPA]/[IB]	[MPPA]/[IBA]	Time (min)	Yield (mol %)[b] IB	IBA	IBX
1[c]		41	0.44	0.44	0.12
1.97[c]		48	0.09	0.68	0.23
	10[d]	31	—	—	0.24

[a] In H_2O–*t*-BuOH 7:3 v/v, pH 7.4, 0.1 M $NaHCO_3$, 21 °C;
[b] Yields are calculated from relative areas of the ^1H NMR signals and that of mesitoate ion;
[c] 0.021 M IB;
[d] 0.01 M IBA.

Table 4. Oxidation of IB by IO_4^-[a]

Time (h)	0	0.68	2.95	25.7	147
10^3 [IB] (M)	10.6	9.94	9.65	6.78 (3)[b]	1.22 (0.7)[b]

[a] In H_2O, pH 6.1, 21.4 °C with initially 0.1 M $NaIO_4$ and 5×10^{-3} M mesitoate ion;
[b] Values in parentheses are [IBA]/[IBX].

and some of the disulfide could have formed by air oxidation.

o-Iodobenzoate ion is oxidized to IBA and then to IBX by MPPA [Table 3, and Fig. 3 (B)]. As in other experiments, extents of the reaction were estimated from signal areas relative to that of mesitoate ion. In the experiment illustrated in Fig. 3 (B) there was some residual peroxyphthalate with a signal at ca. 7.70, m, and another signal under that of phthalate ion.

With equimolar reactants there was no loss of aromatic iodine compounds, but the situation was different with more concentrated MPPA and IBA (Table 3). With 0.01 M IBA and 0.1 M MPPA we saw no ^1H NMR signals of IBA after 31 min at 21 °C, and areas of signals of IBX were only 24% of those of the original IBA (Table 3). The degradation of IBX by MPPA was greater than with HSO_5^- under similar conditions (Tables 2 and 3). Signals in the aromatic region disappeared and that of *t*-BuOH was so large that we have no information on possible structures of the aliphatic products. Oxidation of ethane thiol by IBA gave the disulfide, rather than the sulfonate, as the final product.[9]

Oxidation of 4-methoxybenzene thiol

The final oxidation product, 4-methoxybenzene sulfonate ion, **7**, survived oxidation,[15] but we detected intermediates in the course of reaction. Initially thiol, **4**, was oxidized to disulfide, **5**, by IBA, and intermediate, **6a**, appeared, probably by oxidation of disulfide, **5**. On addition of HSO_5^- a second intermediate, **6b**, appeared at the expense of **6a**. (Fig. 2), and sulfonate, **7**, was formed.

A possible reaction sequence is shown in Scheme 2, in which disulfide is oxidized to the thiol arenesulfinate, **6a**, and HSO_5^- oxidizes **6a** to the thiol arenesulfonate, **6b**. The sulfonate, **7**, could be generated by hydrolyses of **6a,b**, which would reform thiol, **4**, and **4** would be recycled oxidatively. Alternatively the esters **6a,b** could be oxidized to anhydrides which would be rapidly hydrolyzed to an arenesulfinate ion (which would then be rapidly oxidized), or to **7**. Our hypothesis that **6a** is a sulfinate and **6b** a sulfonate is consistent with the latter having higher chemical shifts (Fig. 2), but we recognize that these assignments are speculative.

We did not see ^1H NMR signals of **6a,b** in reactions with MPPA (Fig. 3), consistent with the formation of sulfinate or sulfonate esters, which would react rapidly with a nucleophilic peroxyphthalate dianion to readily give hydrolyzable mixed anhydrides. These reactions would not occur with HSO_5^- which is a weak nucleophile.

The postulated reaction sequence is shown in Scheme 2, although the overall reactions probably include hydrolyses of **6a,b**. The scheme includes the observed chemical shifts, ppm, (Fig. 2).

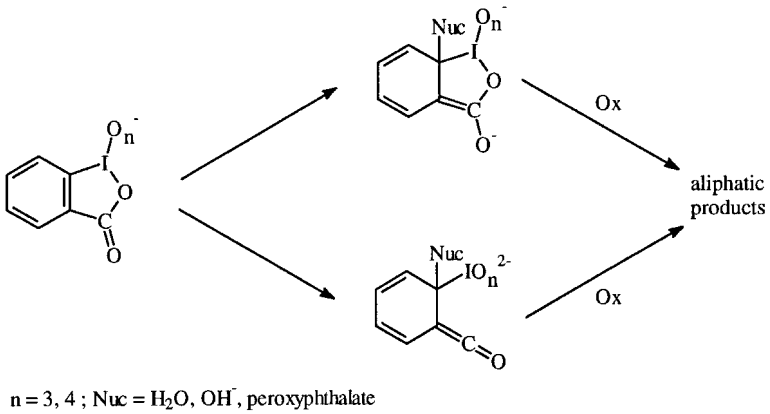
Decomposition of IBX

We did not observe quantitative formation of IBX starting from either IBA or IB and oxidant, because ^1H signals in the aromatic region decreased with time and finally disappeared, indicating that IBX reacts with both HSO_5^- and MPPA. Reaction probably involves further oxidation at iodine, although such an intermediate must be short-lived, because we saw no new ^1H NMR signals.

We considered a reaction in which a hypervalent iodine compound is hydrolyzed to salicylate ion, but we did not see its ^1H NMR signals at 7.88, d, 7.40, t, and 6.92, m, and there was no diminution of these signals relative to those of mesitoate, when salicylate ion, 0.02 M, was left with 0.2 M HSO_5^- for 1 day at 21.4 °C in H_2O–*t*-BuOH 7:3 v/v, pH 7.4. Iodobenzene was oxidized by HSO_5^- to iodoxybenzene [Fig. 3 (A)]. In the reaction conditions used for salicylate ion, and with mesitoate ion as a quantitative marker, there was 70% reaction after 1 h at 21 °C, with no loss of aromatic signals and after 3.7 h we saw only signals of iodoxybenzene at 8.04, d, 2H 7.78, m, 3H. With 0.02 M reactants

$$\underset{\mathbf{4},\ \delta = 7.30, 6.79}{2ArSH} \longrightarrow \underset{\mathbf{5},\ \delta = 6.91, 7.37}{ArSSAr} \longrightarrow \underset{\mathbf{6a},\ \delta = 7.31, 6.44}{ArSO.SAr} \longrightarrow \underset{\mathbf{6b},\ \delta = 7.54, 7.01}{ArSO_2.SAr} \longrightarrow \underset{\mathbf{7},\ \delta = 7.79, 7.04}{2ArSO_3^-}$$

Scheme 2



n = 3, 4 ; Nuc = H_2O, OH^-, peroxyphthalate

Scheme 3

in the above conditions we saw the same ^{1}H NMR signals and 3%, 13% and 13% reaction after 0.1, 2 and 22 h, respectively, probably because HSO_5^- gradually decomposed. There was no decrease in the ^{1}H aromatic signals relative to that of mesitoate ion.

These observations indicate that the acyl residue is involved in the decomposition of IBX. The carbonyl group in the cyclic form of IBX (and IBA) is conjugated with the aromatic residue and a hypervalent iodo compound generated by oxidation of IBX could lose its aromatic character. Possible reactions, shown in Scheme 3 would generate dienes which should react with peroxy acids to form aliphatic compounds. We could not identify ^{1}H NMR signals of these hypothetical products because of the very large signal of the CH_3 groups of *t*-BuOH, and we have no evidence on the step-wise or concerted nature of the hypothetical reactions shown in Scheme 3.

Reaction of periodate ion and IB

Periodate ion oxidizes aryl sulfides,[7] although it is less reactive than HSO_5^- in these reactions,[5b,16] and we examined its reaction with IB at 21.4 °C. The experiment was made with 0.1 M $NaIO_4$ and 0.011 M IB in H_2O, initial pH = 6.4, and 0.005 M mesitoate ion as reference. The solution was unbuffered because $NaHCO_3$ salted out the reactants. The reaction was slow, $t_{1/2} \approx 4\frac{1}{2}$days, but ^{1}H NMR signals of IB decreased and those of IBA and IBX appeared. With time there was some precipitation, probably of *o*-iodoso and *o*-iodoxy benzoic acid. From the relative peak areas of IB and mesitoate ion k_{obs} was 2×10^{-6} s^{-1} and the reaction was too slow to be practically useful. There was slow oxidation by KIO_4 but reactants were not completely soluble.

CONCLUSIONS

Both HSO_5^- and peroxyphthalate ion allow IBA and IBX to be used as turnover catalysts of hydrolysis of activated phosphorus (V) esters and sulfonyl fluorides at mildly alkaline pH in the presence of sulfides. In these conditions peroxyphthalate ion is an effective dephosphorylating agent. Periodate ion oxidizes *o*-iodobenzoate ion, but this reaction is too slow to be practically useful. There is considerable decomposition of aromatic iodine compounds with [peroxyacid] >0.1 M.

EXPERIMENTAL

Materials

Magnesium peroxyphthalate (Lancaster), OXONE (Aldrich), IBA (ACROS), iodobenzene (TCI), *o*-iodobenzoic acid (ACROS), and 4-methoxybenzene thiol (ACROS), 4-nitrobenzenesulfonyl fluoride (Aldrich) were used as received and *p*NPDPP had been used in earlier work.[6] The peroxy contents of OXONE and peroxyphthalate, determined iodometrically, were 80% and 73% of theoretical, respectively, and concentrations were corrected accordingly. Solutions were made up with redistilled, deionized water in H_2O–*t*-BuOH 7:3 v/v to allow solubilization of the substrates and oxidation products of the sulfides.

Kinetics

The reaction of 10^{-4} M 4-nitrobenzenesulfonyl fluoride (**1**) in water was followed in an HP 8451 diode array spectrophotometer at 25.0 °C at pH 8.5 (0.1 M $NaHCO_3$ buffer). The sulfonyl fluoride was added in 30 µl MeCN to 3ml of kinetic solution. The reaction was followed at 240–280 nm and in this range values of first-order rate constants, k_{obs}, varied by <2%, except for the fastest reactions where values were within 5%. There is an isobestic point at 258 nm. The turnover catalysis is shown by the values of 10^3 k_{obs} s^{-1}, at 240, 275 and 280 nm, respectively: 1×10^{-4} M **1**, 1×10^{-4} M IBA— 4.16, 4.24, and 4.25; and 2×10^{-4} M **1**, 1×10^{-4} M IBA—

4.44 (4.87), 4.32 (4.95), and 4.42 (4.95). Values in parentheses were with 1.04×10^{-4} M IBA.

We attempted to examine the IBA catalyzed hydrolysis of *p*NPDPP in the presence of PhSH and HSO_5^- (as OXONE). In MeCN–H_2O 3:7 v/v, pH 8.5 (nominal), 0.1 M $NaHCO_3$ buffer and 2.4×10^{-5} M *p*NPDPP, the second-order rate constant for reaction with IBA was 0.56 M^{-1} s^{-1} at 25.0 °C, which is similar to the value of 1.0 M^{-1} s^{-1} at pH 7.0 in water.[10] We could not obtain good kinetic data spectrophotometrically in the presence of OXONE and PhSH, because precipitates formed, although absorbance at 400 nm increased as expected.

We made qualitative observations on the deactivation of IBA using thioanisole, **2**, and its regeneration on addition of HSO_5^- in H_2O–*t*-BuOH 7:3 v/v, pH 8.5, 0.1 M $NaHCO_3$. When 10^{-4} M *p*NPDPP was added to 10^{-3} M IBA at ca. 21 °C the solution became yellow within a few minutes. Addition of 10^{-3} M **2** stopped color development, but it immediately resumed on addition of 2×10^{-3} M HSO_5^-. The color of *p*-nitrophenoxide ion was unaffected by HSO_5^- in these conditions, provided that the pH was maintained.

NMR spectroscopy

Spectra were monitored typically in H_2O–*t*–BuOH 7:3 v/v on a Varian Unity (INOVA) instrument, 400 MHz for ^1H, in isotopically normal solvents with a D_2O insert, TSP as external reference, and suppression of the ^1H signal of H_2O. As a result of signal suppression we saw some 'spikes' in the spectra, which appeared in the absence of reactants and were easily identified. The breaks in NMR spectra were due to these adventitious 'spikes'. There was a large signal of CH_3 of *t*-BuOH and therefore we only monitored signals in the aromatic region. We used mesitoate (2,4,6-trimethylbenzoate) ion, δ_H = 6.86 ppm, s, as a calibrating standard for estimating extents of reaction.[11] The ^{19}F signal of 4-$O_2NC_6H_4SO_2F$ was at −68.5 ppm and that of F^- was at −112.4 ppm, relative to CF_3Cl δ = 0 ppm measured with CF_3CO_2H as an external reference, δ = 76.55 ppm.

There was overlap of some ^1H signals of the iodo compounds and of the oxidation products, but in all conditions there were sufficient ^1H signals to allow quantification of iodo compounds, based on comparison of peak areas with that of mesitoate ion. Chemical shifts varied slightly with changes in the reaction medium because we used external references, but there was no effect on signal multiplicities or relative peak areas. In most compounds that we examined, hydrogens in a given molecule were in 1:1 ratios, which assisted identification. The ^1H NMR signals of the stock compounds are given in Table 1.

Acknowledgements

This work was supported by the US Army Research Office. We are grateful to Professor R. A. Moss for information on the reaction of IBA and IBX with thiols and for his prepublication manuscript.

REFERENCES

1. (a) Y.-C. Yang, J. A. Baker and J. R. Ward, *Chem. Rev.*, **92**, 1729 (1992); (b) Y.-C. Yang, *Chem. Ind. (London)*, 334 (1995); (c) Y.-C. Yang, *Accounts Chem. Res.*, **32**, 109 (1999).
2. R. A. Moss, K. Y. Kim and S. Swarup, *J. Am. Chem. Soc.*, **108**, 788 (1986).
3. (a) A. R. Katritsky, B. L. Duell, H. D. Durst and B. L. Knier, *J. Org. Chem.*, **53**, 3972 (1988); (b) R. S. Hammond, J. S. Forster, C. N. Lieske and H. D. Durst, *J. Org. Chem.*, **111**, 7860 (1989).
4. F. J. Berg, R. A. Moss, Y. C. Yang and H. Zhang, *Langmuir*, **11**, 411 (1995).
5. (a) R. J. Kennedy and A. M. Stock, *J. Org. Chem.*, **25**, 1901 (1906); (b) R. Bacaloglu, A. Blasko, C. A. Bunton and H. Foroudian, *J. Org. Chem.*, **5**, 171 (1992); (c) C. A. Bunton, H. J. Foroudian and A. Kumar, *J. Org. Chem.* **2**, 33 (1995); (d) Y. C. Yang, L. L. Szafraniec, W. T. Beaudry and D. K. Rohrbaugh, *J. Org. Chem.*, **11**, 6621 (1990).
6. C. A. Bunton, M. M. Mhala and J. R. Moffatt, *J. Phys. Org. Chem.*, **3**, 390 (1990); S. Bhattacharya and K. Snehalatha, *J. Phys. Org. Chem.*, **62**, 2198 (1997).
7. F. Ruff and A. Kucsman, *J. Chem. Soc. Perkin Trans* **2**, 683 (1985).
8. C. A. Bunton, H. J. Foroudian, N. D. Gillitt and A. Kumar, ERDEC Conference on Chemical and Biological Defense Abstract November, 1998.
9. R. A. Moss, H. Morales-Rojas, H. Zhang and B. D. Park, *Langmuir*, **15**, 2738 (1999).
10. C. A. Bunton, M. M. Mhala and J. R. Moffatt, *J. Phys. Chem.*, **93**, 854 (1989).
11. R. Bacaloglu, C. A. Bunton, G. Cerichelli and F. Ortega, *J. Am. Chem. Soc.*, **110**, 3495, (1988).
12. R. A. Moss and H. Zhang, *J. Am. Chem. Soc.*, **116**, 4471 (1994).
13. W. Wolf, J. C. J. Chen and L. J. Hsu, *J. Pharm. Sci.*, **55**, 68 (1966).
14. R. A. Moss, K. W. Alwis and G. O. Bizzigotti, *J. Am. Chem. Soc.*, **105**, 681 (1983).
15. Y. C. Yang, L. L. Szafraniec, W. T. Beaudry, C. A. Bunton and A. Kumar, *J. Chem. Soc. Perkin Trans.* **2**, 607 (1997).
16. A. Blasko, C. A. Bunton and S. Wright, *J. Phys. Chem.*, **97**, 5435 (1993).

