



In-situ degradation of sulphur mustard using (1R)-(-)-(camphorylsulphonyl) oxaziridine impregnated adsorbents

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ABSTRACT

Bis-2-chloroethyl sulphide (sulphur mustard or HD) is an extremely toxic and persistent chemical warfare agent. For in-situ degradation of HD and its analogues (simulants), i.e., dibutyl sulphide (DBS) and ethyl 2-hydroxyethyl sulphide (HEES), different adsorbents systems loaded with (1R)-(-)-(camphorylsulphonyl) oxaziridine were prepared. Solution of sulphur mustard and its simulants was prepared in carbon tetrachloride and taken for uniform adsorption on the impregnated systems using incipient volume. Degradation kinetics monitored by GC/FID were found to be first-order. The half-life of degradation reactions for simulants was obtained in less than 30 and for HD in 120 min. From the studied kinetics it was observed that reaction was very rapid with simulants and decreased rate was found for HD. The order of reactivity of MgO/Oxa system for HD and simulants was found to be DBS > HEES > HD. Reaction products of the oxidation reaction of simulants and HD on adsorbents were extracted in dichloromethane and analysed by GC-MS. The products were found to be non-toxic sulphoxide. The objective of the study is to develop a reactive adsorbent for in-situ degradation of sulphur mustard which could be used in nuclear biological and chemical (NBC) filtration systems.

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1. Introduction

Bis(2-chloroethyl) sulphide (sulphur mustard or HD) is a strong vesicant and has been employed as a chemical warfare (CW) agent. HD persists in the environment for long periods because of its low volatility and slow rate of decomposition. HD is highly reactive bifunctional compound and has been documented as mutagenic, antimetabolic, carcinogenic, teratogenic and cytotoxic agent [1,2]. The reactivity of HD is determined by central sulphur atom as well as by the side chains. Oxidation is a typical example where the central atom is subjected to electrophilic attack leading to the formation of sulphone and sulphoxides. Another way of reaction is the formation of sulphonium salts by electrophilic attack [3–8]. The physicochemical characteristic of HD is presented in Table 1.

HD decontamination is very difficult and becomes a major challenge for the researchers and army. Several methods have been developed for the liquid decontamination. It is decontaminated by using oxidants such as $3\text{Ca}(\text{ClO})_2 \cdot 2\text{Ca}(\text{OH})_2$, DS-2, hydrogen peroxide, nitric acid, potassium permanganate, chromic acid, and hypochlorites [9,10]. Low solubility of the CW agents, toxicity, and corrosive properties are the limitation with the liquid decontami-

nation. Alternatively, researchers have been using solid adsorbents such as Fuller's earth, XE-555, bleaching powder, and modified resins for the decontamination applications [11–13]. Although these adsorbents remove the agents from contaminated surfaces physically, they do not detoxify the agents even after several days due to lack of reactivity.

Sorbents which are not only adsorbed CW agents but also degrade them such as inorganic oxide such as MgO, CaO, and Al_2O_3 are used for decontamination of CW agents and is a current subject utilizing for research. Nanosize MgO, γ -alumina, polydivinylbenzene, nanosize CaO [14–18] were also used for the detoxification reaction. HD, [O-ethyl S-(2-diisopropylamino) ethyl methyl phosphonothionate] (VX), were found to react with CaO [19], MgO [18], nanosize alumina [20] and zeolites [21].

In the present study we checked the degradation capability of adsorbent and impregnated adsorbent against HD. For impregnation (1R)-(-)-(camphorylsulphonyl) oxaziridine was selected. It is a heterocyclic compounds containing oxygen, nitrogen and carbon atoms in a three-membered ring. It is a highly reactive molecule and displays novel and unusual chemistry [22,23]. These are aprotic oxidising agents capable of selectively oxidising sulphides and disulphides to sulphoxides and thiosulphinates without over oxidation. Adsorbents impregnated with (1R)-(-)-(camphorylsulphonyl) oxaziridine were tested for reactivity against HD and its stimulants. Kinetics of degradation of HD and its stimulants were studied on the most reactive adsorbent. Rate constant and half life of the reac-

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Table 1
Physicochemical properties of HD.

| S. no. | Physicochemical properties of HD | |
|--------|----------------------------------|--|
| 1 | Chemical formula | Bis(2-chloroethyl) sulphide |
| 2 | Molecular weight | 159.08 |
| 3 | Melting point | 13–14 °C |
| 4 | Boiling point | 215–217 °C |
| 5 | Vapour pressure (20 °C) | 0.11 mmHg |
| 6 | Density (20 °C) | 1.27 g cm ⁻³ |
| 7 | Solubility in water | 0.8 g/L |
| 8 | Vapour pressure (20 °C) | 0.115 mmHg |
| 9 | Vapour density | 5.4 |
| 10 | Solubility in organic solvents | Highly soluble except in petroleum ether |

tion were calculated. Reaction products were also analysed and identified as sulphoxides.

2. Experimental

2.1. Materials

Active carbon of coconut shell origin, particle size 12 × 30 BSS (British sieve size) was procured from M/S Active Carbon India Ltd., Hyderabad. Sulphur mustard was obtained from Synthetic Chemistry Division of our establishment. Chloroform (AR grade), carbon tetrachloride, dichloromethane, dibutyl sulphide, ethyl 2-hydroxyethyl sulphide, magnesium oxide, alumina, camphorylsulphonylimine, toluene, potassium carbonate, potassium mono peroxy sulphate, sodium sulphide, magnesium sulphate and n-pentane were obtained from E-merk India Ltd., SD fine India, Lancaster, UK. Caution: sulphur mustard and its simulants are highly toxic.

2.2. Preparation of (1R)-(–)-(camphorylsulphonyl) oxaziridine

(1R)-(–)-(camphorylsulphonyl) oxaziridine was prepared by using standard method and characterized using NMR in CDCl₃. For the preparation of (1R)-(–)-(camphorylsulphonyl) oxaziridine, solution of camphorylsulphonylimine and potassium carbonate was prepared by dissolving 8.2 mmol in 80 mL toluene and 9.5 g in 50 mL water, respectively. These two solutions were taken in round bottom flask containing magnetic bead. The reaction was stirred vigorously and a solution of potassium mono peroxy sulphate (6.0 g) in 50 mL water was added drop wise within 15 min. The formation of (1R)-(–)-(camphorylsulphonyl) oxaziridine was monitored by NMR. After completion of reaction, the aqueous layer was separated and washed with 25 mL toluene. The organic layer was washed with 25 mL of aqueous 10% sodium sulphide and dried over anhydrous magnesium sulphate and solvent was evaporated below 40 °C. The viscous oily liquid was obtained. Oxaziridine was precipitated out by n-pentane [23].

2.3. Preparation of impregnated adsorbents

(1R)-(–)-(camphorylsulphonyl) oxaziridine was loaded on various adsorbents such as carbon, magnesium oxide and alumina. Solution of (1R)-(–)-(camphorylsulphonyl) oxaziridine (10.0%, w/w) was prepared in chloroform and impregnated using incipient wetness technique [24]. As per this technique, solution was added to the adsorbent slowly by mixing the adsorbent to avoid heterogeneous deposition of impregnants. Impregnated adsorbents were dried at 50 °C for 4 h.

2.4. Screening of adsorbents

100 mg impregnated adsorbents were placed in glass tube with 50 µL solution containing 3 µL HD or DBS or HEES in carbon tetra-

chloride. The test tubes were sealed and allowed to stand at room temperature. After 24 h they were extracted with solvent and the supernatant solutions were analysed by GC/FID. The adsorbent systems which were found reactive, studied for reaction kinetic.

2.5. Reaction procedure

All the reactions were carried out in glass tubes. 100 mg impregnated adsorbents were placed in glass tube containing 50 µL solution containing 3 µL HD or DBS or HEES in carbon tetrachloride. These tubes containing the reaction mixture were allowed to stand at room temperature and each tube was taken out for kinetics studies at regular intervals of time. For kinetics of degradation, residual toxicants were extracted in carbon tetrachloride and the solutions were subjected to GC/FID analysis using splitless injection technique. GC spectra were obtained periodically to monitor the reaction in-situ. All gas chromatographic analysis was performed on a Chemito 8610 gas chromatograph equipped with BP5 column (5% phenyl methyl silicon capillary column of 30 ft. length, 0.3 mm internal diameter) and flame ionization detector (FID). Isothermal method was adopted for GC analysis, the oven, injection port and detector were kept at 120, 220, 250 °C respectively. Caution: The experiments were performed carefully using applicable safety procedures. All the experiments were performed in the fume cupboard.

2.6. Characterization of reaction products

For products, 500 mg of MgO/Oxa system was taken in the test tubes. 50 µL solvent containing 10 µL toxicants were dropped in the MgO/Oxa system. After 24 h, samples were extracted by stirring in 3.0 mL of dichloromethane for 60 min in a well-stoppered test tube. The mixture was then centrifuged, transferred to another tube, concentrated by N₂ purging and analysed by GC/MS for reaction products. GC/MS of Agilent make 5973N MSD (inert) equipped with HP-5 MS column of 30 m × 0.25 mm × 0.25 µm was used. Electron impact ion source (70 eV electron impact energy) and quadrupole analyser were maintained at 150 °C while injection port and GC/MS interface kept at 280 °C. GC/MS was used in temperature programming mode from 50 to 280 @ 10 °C/min.

3. Result and discussion

The (1R)-(–)-(camphorylsulphonyl) oxaziridine was loaded on different adsorbents such as carbon, MgO and Al₂O₃. The surface areas were determined using Autosorb 1C from Quantachrome, USA and found to be 1250, 45.5 and 105.8 m²/g, respectively. These impregnated adsorbents were tested for reactivity against HD, DBS and HEES. Different behaviour of reactions was observed on all the three impregnated adsorbents. Carbon alone did not participate in the degradation reaction of HD and carbon supported oxaziridine was also not found to be reactive against toxicants. This indicates that oxaziridine became inactive after interaction with carbon. So carbon was not the suitable support for oxaziridine. In case of alumina supported oxaziridine, alumina (without impregnant) was found to be more reactive than impregnated alumina. Support itself (Al₂O₃) behaved as reactive sorbent. From this observation, it was observed that oxaziridine did not enhance the reactive power of alumina in turn it showed the negative effect. MgO was impregnated in same manner and analysed. The results indicated that MgO alone did not found to be reactive against toxicants but MgO impregnated with oxaziridine (MgO/Oxa) was found to be reactive in the degradation of HD.

After screening of adsorbents, the kinetics of degradation of HD and its stimulants were studied. For this, solution of actual agent (HD) and its stimulants was prepared in carbon tetrachloride and

incipient volume was taken on MgO/Oxa for homogeneous distribution of the toxic chemicals (100 mg MgO containing 3 μ L toxicant in 50 μ L carbon tetrachloride). After definite time intervals, residual toxicants were extracted in carbon tetrachloride and the solutions were subjected to GC/FID analysis. Kinetic plots are made by taking $\log(a-x)$ on Y-axis and time on X-axis [25] and is depicted in Fig. 1 where a is the initial concentration and x is the degraded amount. The linear curves (Fig. 1) indicated that the reactions follow first-order rate equation. Rate constant was calculated using the slope of the straight line drawn. Half-life of reactions was calculated from $0.6932/k$. MgO/Oxa degraded 27% of HD in 60 min. The rate constant value was found to be $6.6 \times 10^{-3} \text{ min}^{-1}$ and half-life of reaction to be 105 min.

From the studied kinetics it was observed that reaction was very rapid with simulants and decreased rate was found for HD. The order of reactivity of MgO/Oxa for HD and simulants was found to be DBS > HEES > HD. The ease of oxidation of sulphides depends on the nucleophilicity of the sulphur atom. In case of HD, sulphur atom is oxidatively less reactive than DBS and HEES because of the presence of electron withdrawing chlorine atoms. HEES is having hydroxyl group, which is also a electron withdrawing group but

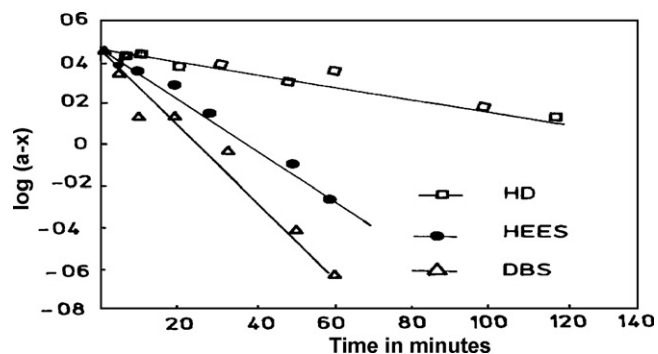


Fig. 1. Kinetic of degradation of HD, HEES and DBS on MgO/Oxa systems.

less strong to chlorine atoms so HEES degradation was found to be faster than HD. The most reactive sulphide for oxidation was found to be DBS as no electron withdrawing groups are present in it. Degradation products were found to be sulphoxide in all the three cases [26].

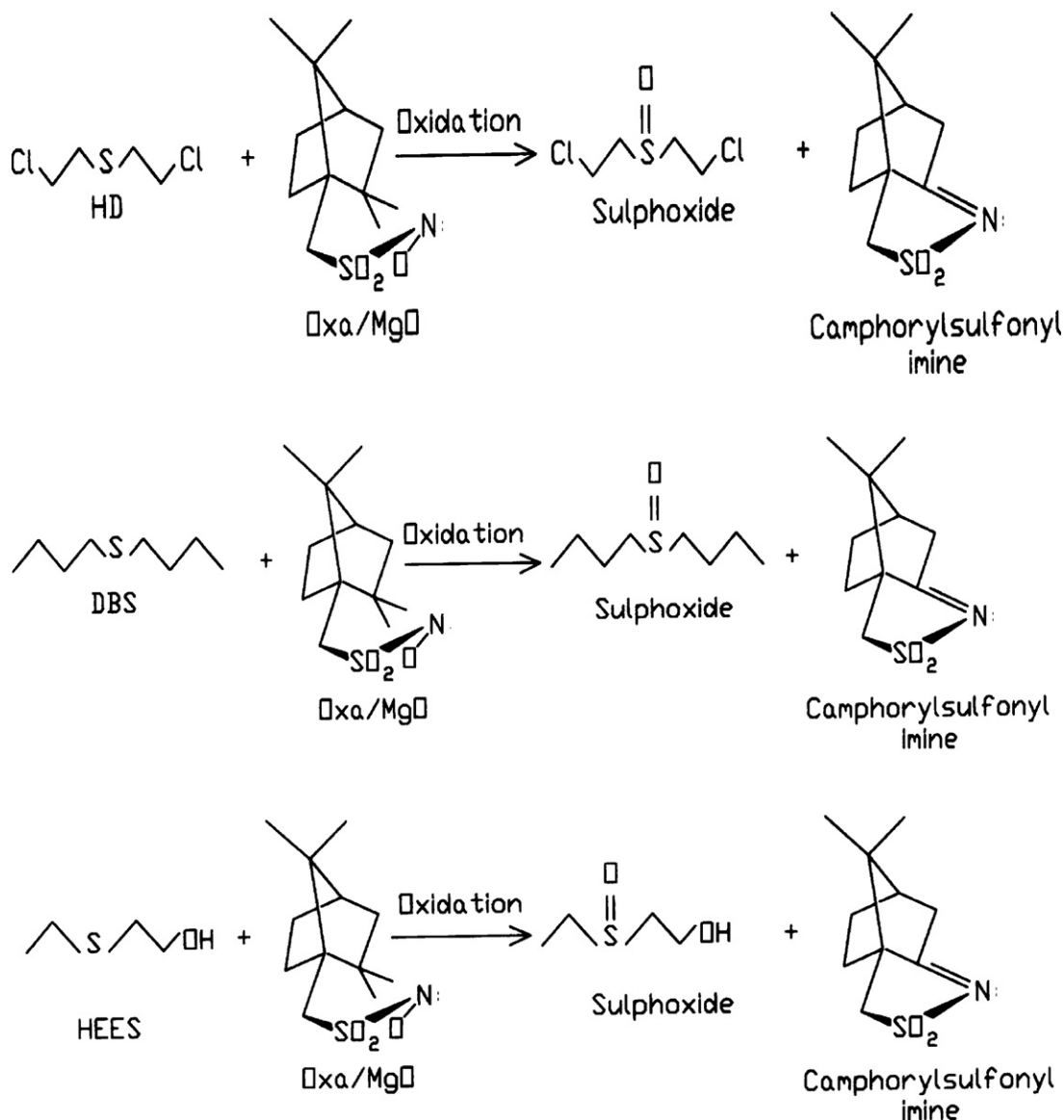


Fig. 2. Reaction of HD, DBS and HEES on Oxa/MgO.

3.1. Reaction schemes

The oxidation of sulphides by oxaziridine is a nucleophilic type attack by the sulphides on the electrophilic oxygen atom of the oxaziridine. The SN^2 mechanism was previously reported for sulphides [27]. Fig. 2 describes the oxidation reaction for the formation of sulphoxide with HD, HEES and DBS.

4. Conclusions

(1R)-(–)-(camphorylsulphonyl) oxaziridine was loaded on carbon, alumina and magnesium oxide. In screening (1R)-(–)-(camphorylsulphonyl) oxaziridine loaded on magnesium oxide was found to be reactive sorbent for the degradation of sulphur mustard and its analogues. On this system kinetics of degradation of toxicants were studied and found to be followed the first-order rate equation. The degradation reaction was fast with DBS and HEES and half-life values were obtained in less than 30 min. HD was degraded half of the initial amount in 105 min. The reactivity order for the oxidation reaction was found to be DBS > HEES > HD. Degradation products were analysed by GC/MS and found to be sulphoxide.

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References

- [1] A.P. Watson, G.D. Griffin, Toxicity of vesicant agents scheduled for destruction by the chemical stockpile disposal program, *Environ. Health Perspect.* 98 (1992) 259–280.
- [2] G.P. Wheeler, Studies related to the mechanism of action of cytotoxic alkylating agents, *Ann. Rev. Cancer Res.* 22 (1962) 1–88.
- [3] P.D. Barlett, C.G. Swain, Kinetics of hydrolysis and displacement reactions of beta, beta1-dichlorodiethyl sulfide (mustard gas) and of beta-chloro-beta-hydroxy diethyl sulfide (mustard chlorohydrin), *J. Am. Chem. Soc.* 71 (1949) 1406–1415.
- [4] Y.C. Yang, L.L. Szafraniec, W.T. Beaudry, J.R. Ward, Kinetics and mechanisms of the hydrolysis of 2-chloroethyl sulfides, *J. Org. Chem.* 53 (1988) 3293–3297.
- [5] Y.C. Yang, J.R. Ward, T. Luteran, Hydrolysis of mustard derivatives in aqueous acetone–water and ethanol–water mixtures, *J. Org. Chem.* 51 (1986) 2756–2759.
- [6] F.L. Hsu, L.L. Szafraniec, W.T. Beaudry, Y.C. Yang, Oxidation of sulphur mustard to sulphoxides by dimethylsulfoxide, *J. Org. Chem.* 55 (1990) 4153–4155.
- [7] Y.C. Yang, J.A. Baker, J.R. Ward, Decontamination of chemical warfare agents, *Chem. Rev.* 92 (1992) 1729–1743.
- [8] Y.C. Yang, L.L. Szafraniec, W.T. Beaudry, A comparison of the oxidative reactivities of mustard (2,2'-dichlorodiethyl sulfide) and bivalent sulphoxides, *J. Org. Chem.* 55 (1990) 3664–3666.
- [9] S. Franke, *Lehrbuch der Militäarchemie*, vol. 1, Militäerverlag der DDR, Berlin, 1977.
- [10] S. Popiel, Z. Witkiewicz, Al. Szewczuk, The GC/AED studies on the reactions of sulfur mustard with oxidants, *J. Hazard. Mater.* 123 (2005) 94–111.
- [11] R.P. Chilcott, J. Jenner, W. Carrick, S.A.M. Hotchkiss, P. Rice, Human skin absorption of bis-2-(chloroethyl)sulphide (sulphur mustard) in vitro, *J. Appl. Toxicol.* 20 (2000) 349–355.
- [12] R.P. Chilcott, J. Jenner, S.A.M. Hotchkiss, P. Rice, In vitro skin absorption and decontamination of sulphur mustard: comparison of human and pig-ear skin, *J. Appl. Toxicol.* 21 (2001) 279–283.
- [13] P. Kumar, U.S. Sharma, R. Vijayaraghavan, Study of the efficacy of CC-2 and Fuller's Earth Combination as a decontaminant against sulphur mustard (mustard gas) dermal intoxication in mice, *Def. Sci. J.* 41 (1991) 363–366.
- [14] G.W. Wager, P.W. Bartram, Reactions of the nerve agent simulant diisopropyl fluorophosphate with self-decontaminating adsorbents A ^{31}P MAS NMR study, *J. Mol. Catal. A: Chem.* 144 (3) (1999) 419–424.
- [15] G.W. Wagner, O.B. Koper, E. Lucas, S. Decker, K.J. Klabunde, Reactions of VX, GD, and HD with nanosize CaO: autocatalytic dehydrohalogenation of HD, *J. Phys. Chem. B* 104 (21) (2000) 5118–5123.
- [16] O. Koper, K.J. Klabunde, Nanoparticles for the destructive sorption of biological and chemical contaminants, U.S. Patent 6,057,488, May 2, 2000.
- [17] S. Rajagopalan, O. Koper, S. Decker, K.J. Klabunde, Nanocrystalline metal oxides as destructive adsorbents for organophosphorus compounds at ambient temperatures, *Chem. A Eur. J.* 8 (2002) 2602–2607.
- [18] R.M. Narske, K.J. Klabunde, S. Fultz, Solvent effects on the heterogeneous adsorption and reactions of (2-chloroethyl) ethyl sulfide on nanocrystalline magnesium oxide, *Langmuir* 18 (2002) 4819–4825.
- [19] G.W. Wagner, P.W. Bartram, O. Koper, K.J. Klabunde, Reactions of VX, GD, and HD with nanosize MgO, *J. Phys. Chem. B* 103 (16) (1999) 3225–3228.
- [20] G.W. Wagner, L.R. Procell, R.J. O'Connor, S. Munavalli, C.L. Carnes, P.N. Kapoor, K.J. Klabunde, Reactions of VX, GB, GD, and HD with nanosize Al_2O_3 , formation of aluminophosphonates, *J. Am. Chem. Soc.* 123 (8) (2001) 1636–1644.
- [21] G.W. Wager, P.W. Bartram, Reactions of VX, HD, and their simulants with NaY and AgY zeolites. Desulfurization of VX on AgY, *Langmuir* 15 (1999) 8113–8118.
- [22] R.D. Bach, B.A. Coddens, J.J.W. McDouall, H.B. Schlegel, The mechanism of oxygen transfer from an oxaziridine to a sulfide & sulfoxide: a theoretical study, *J. Org. Chem.* 55 (1990) 3325–3330.
- [23] F.A. Davis, J.C. Towson, M.C. Weismiller, S. Lal, P.J. Carroll, Chemistry of oxaziridines. 11. (Camphorylsulfonyl) oxaziridines; synthesis & properties, *J. Am. Chem. Soc.* 110 (1988) 8477–8482.
- [24] B. Singh, S. Madhusudanan, C.G. Padma Kumar, S.R.S. Sachan, S.K. Pandey, S. Agarwal, Determination of copper, total chromium and silver in impregnated carbon, *Def. Sci. J.* 48 (4) (1998) 365–369.
- [25] S.H. Maron, C.F. Prutton, Principles of Physical Chemistry, 4th ed., Amerind Publishing Co. Pvt. Ltd., New Delhi, 1972.
- [26] F.A. Davis, R.H. Jenkins, S.G. Yocklovich, 2-Arenesulfonyl-3-aryloxaziridines—new class of aprotic oxidizing-agents (oxidation of organic sulfur-compounds), *Tetrahedron. Lett.* 52 (1978) 5171–5174.
- [27] F.A. Davis, J.M. Billmers, D.J. Gosciniak, J.C. Towson, Chemistry of oxaziridines 7'. Kinetics and mechanism of the oxidation of sulfoxides and alkenes by 2-sulfonyloxaziridines. Relationship to the oxygen-transfer reactions of metal peroxides, *J. Org. Chem.* 51 (1986) 4240–4245.