Sparapani for skilful experimental help.

Marina Attinà, Fulvio Cacace,* **Pierluigi Giacomello**
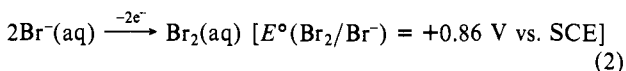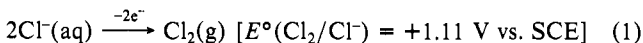*University of Rome, 00100 Rome, Italy*

Maurizio Speranza
Istituto di Chimica Nucleare del C.N.R.
00016 Monterotondo Stazione, Rome, Italy
Received March 12, 1980

Visible Light Driven Generation of Chlorine and Bromine. Photooxidation of Chloride and Bromide in Aqueous Solution at Illuminated n-Type Semiconducting Molybdenum Diselenide and Molybdenum Disulfide Electrodes

Sir:

We report the sustained, visible light driven oxidation of Br^- and Cl^- according to eq 1 and 2 in aqueous solutions with the use of n-type semiconducting MoY_2 (Y = S, Se) photoanode-based

$$2Cl^-(aq) \xrightarrow{-2e^-} Cl_2(g) \quad [E^\circ(Cl_2/Cl^-) = +1.11 \text{ V vs. SCE}] \quad (1)$$

$$2Br^-(aq) \xrightarrow{-2e^-} Br_2(aq) \quad [E^\circ(Br_2/Br^-) = +0.86 \text{ V vs. SCE}] \quad (2)$$

cells. On the basis of results from previous studies, the oxidizing power of the photogenerated holes at the MoY_2/liquid interface is great enough [more positive than $E^\circ(Cl_2/Cl^-)$] to effect Cl_2 or Br_2 generation in aqueous solution.[1–3] However, in aqueous solutions, photoanodic corrosion of the electrodes is the dominant process in the presence of Br^- or Cl^-,[1–3] while photooxidation of I^- to I_3^- has been shown to be quite efficient at MoY_2 photoanodes in aqueous media.[3,4] This investigation of the oxidation of aqueous Cl^- and Br^- was prompted by the findings in this laboratory that Cl^-, Br^-, or I^- could be photooxidized in nonaqueous (CH_3CN) solution without deterioration of the MoY_2 photoanode.[5–7] We thus sought conditions where the oxidation of Cl^- or Br^- could be achieved in aqueous solutions, starting with the notion that the solvent (H_2O) could play both the role of (i) kinetic competitor with X^- for the photogenerated oxidizing equivalents and (ii) partially determining the energetics for the photocorrosion process.[8–10]

Our strategy for oxidation of Cl^- or Br^- in aqueous solution has been to employ super high concentrations of these ions by using aqueous electrolyte solutions of LiCl (15 M) or LiBr (12 M). The rationale is twofold: (i) the effective activity of X^- can be much higher than the concentration (the Cl^- activity of 15 M LiCl is
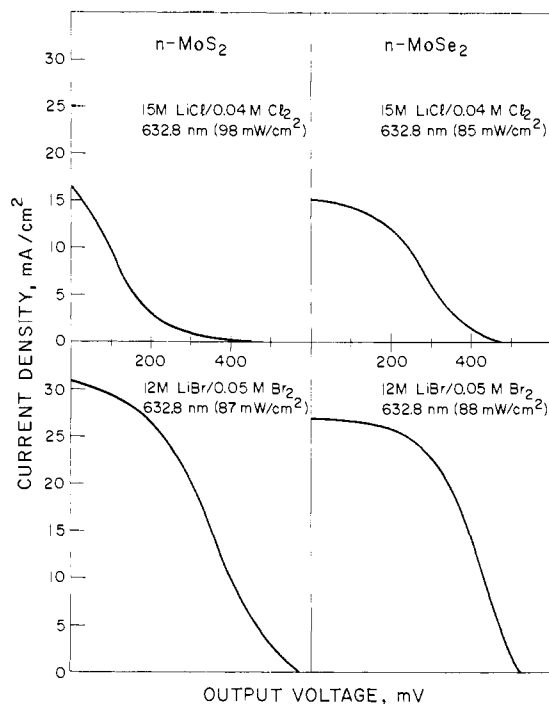
$\sim$480 M and the Br^- activity of 12 M LiBr is $\sim$560 M[11]) to provide the kinetic advantage for productive photooxidation of X^-, and (ii) the activity of H_2O can be reduced significantly by the high ionic strength[11] to reduce the efficiency for photocorrosion.

Visible light irradiation of the single-crystal, n-type MoY_2 anode of an electrochemical cell employing aqueous 15 M LiCl or 12 M LiBr (pH $\approx$6) results in the anodic processes represented by eq 1 or 2, respectively.[12] Light of higher energy than the band gap, $\sim$1.1 eV, is effective.[13,14] Quantitative measurements have been made by using 514.5- or 632.8-nm light from an Ar ion or He–Ne laser, respectively. The cathode process is either the reduction of X_2 to $2X^-$ and/or the reduction of H_2O to form H_2, depending on the amount of X_2 present.

Two facts are significant. First, the photoanodes are durable when X_2 is being generated. Second, photooxidation occurs at MoY_2 potentials up to $\sim$0.5 V more negative than $E^\circ(X_2/X^-)$, showing that light can contribute up to $\sim$0.5 V toward the energy needed to produce X_2. Steady-state photocurrent–voltage curves for MY_2 photoanodes in X_2/LiX aqueous solutions are given in Figure 1. Under these conditions, the dark Pt cathode process is X_2 to $2X^-$ reduction, and there is no net chemical change in the cell. Data from such curves are summarized in Table I. When the MoY_2 potential is more negative than the electrochemical

Figure 1. Steady-state photocurrent–voltage curves for n-type MoS_2 (left frames) and n-type $MoSe_2$ (right frames) photoanode-based cells. Illumination was at 632.8 nm under the conditions indicated.

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(12) Electrodes were prepared by using materials and procedures previously described.[5–7] LiCl and LiBr solutions were prepared by adding distilled H_2O to the solid to achieve a concentration of 15 M LiCl and 12 M LiBr. Small amounts of insoluble materials were filtered to achieve optical clarity. Solutions for steady-state photocurrent–voltage curves were prepared by adding Cl_2 or Br_2 to the LiCl or LiBr, respectively, and were stoppered to prevent escape of the X_2 from the electrochemical cell. All data are for 298 K. Samples of photogenerated gas (Cl_2) or authentic Cl_2 were added to a 9 mM $IrCl(CO)(PPh_3)_2$ (from Pressure Chemical Co.) $CHCl_3$ solution under Ar via a gas-tight Hamilton syringe with Teflon fittings. Infrared spectra of $IrCl(CO)(PPh_3)_2$ and $IrCl_3(CO)(PPh_3)_2$ were obtained by using a Perkin-Elmer Model 180 spectrometer. Br_2 was monitored spectrophotometrically with a Cary 17 UV–vis–near-IR spectrophotometer.
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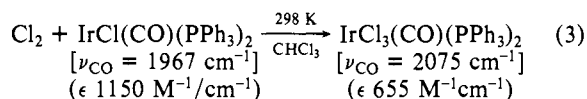(14) Kautek, W.; Gerischer, H.; Tributsch, H. *J. Electrochem. Soc.* **1980**, *128*.

Communications to the Editor

J. Am. Chem. Soc., Vol. 102, No. 22, 1980 6899

Table I. Output Characteristics for n-Type MoS_2- and $MoSe_2$-Based Photoelectrochemical Cells

electrolyte	photo-anode	input, mW/cm² ^{a}	$\Phi_e{}^b$	max power output, mW/cm²	max V (V at $\eta_{max})^c$	η_{max} %^{d}	fill factor^e
H_2O, 15 M LiCl, 0.04 M Cl_2 (E_{redox} = 1.03 V vs. SCE)	$MoSe_2$	28	0.51	0.87	400 (190)	3.1	0.30
		85^f	0.35	2.4	480 (230)	2.9	0.34
		160	0.50	5.6	530 (230)	3.5	0.26
	MoS_2	27	0.29	0.2	400 (110)	0.7	0.29
		98^f	0.34	1.0	450 (110)	1.1	0.34
		270	0.28	4.2	520 (170)	1.6	0.28
H_2O, 12 M LiBr, 0.05 M Br_2 (E_{redox} = 0.69 V vs. SCE)	$MoSe_2$	7.3	0.60	0.51	410 (280)	7.0	0.60
		29	0.61	2.1	480 (300)	7.5	0.61
		88^f	0.61	6.9	530 (320)	7.9	0.61
		160	0.62	12	570 (320)	7.8	0.62
	MoS_2	7.2	0.69	0.45	460 (240)	6.2	0.69
		28	0.68	2.1	520 (300)	7.4	0.68
		87^f	0.69	6.1	570 (280)	7.0	0.69
		160	0.70	11	600 (280)	7.2	0.70

^{a} Input power is the 632.8-nm line from a Coherent Radiation He–Ne laser. ^{b} Quantum yield for electron flow at E_{redox}; this corresponds to the short-circuit quantum yield taken as the number of electrons passed per incident photon. ^{c} Maximum voltage is the open-circuit photopotential, and the number in parentheses is the output voltage at the maximum power point. ^{d} Efficiency for the conversion of 632.8-nm light to electricity. ^{e} Fill factor is a measure of the rectangularity of the current–voltage curves (Figure 1) and is defined as the max power/(max V × short-circuit photocurrent).

potential of the solution, light is converted to electricity when there is photocurrent. Efficiencies[15] for the conversion of 632.8-nm light to electricity are given in Table I. The approximately 7% efficiencies for X = Br are among the highest ever reported from this laboratory[5-7] under any conditions for the MY_2 photoanodes.[16] The large difference in efficiency for Cl^- and Br^- photooxidation at MoS_2 may reflect a strong interaction with the Br^-. The efficiencies show no significant dependence on input light intensity over the range used. It is noteworthy that the light intensity from the AM1 solar spectrum is only ~100 mW/cm² and that the Cl_2/Cl^- and Br_2/Br^- couples are more transparent than the I_3^-/I^- couple that has previously been used in durable photoelectrochemical cells for conversion of visible light to electricity.[4,6,7,16c,17-19]

The durability of the photoanodes is first suggested by noting that there is no obvious surface corrosion after photoelectrolytic oxidation of X^-, with or without added X_2. When the LiX concentration is only 0.1 M, the rapid surface photocorrosion is obvious on the time scale of doing experiments such as those represented in Figure 1 and Table I. Current efficiency for Cl_2 generation from 15 M LiCl was measured for the MoY_2 photoanodes by collecting the Cl_2 gas (up to 15 mL) above the photoanode by using an inverted graduated pipette. The Cl_2 was found to be the gaseous product by smell, color, and reaction with $CHCl_3$ solutions of $IrCl(CO)(PPh_3)_2$ as compared with an authentic sample of Cl_2 gas. The reaction of Cl_2 with $IrCl(CO)(PPh_3)_2$ proceeds according to eq 3 and can be used to quantitate

$$Cl_2 + IrCl(CO)(PPh_3)_2 \xrightarrow[CHCl_3]{298\ K} IrCl_3(CO)(PPh_3)_2 \quad (3)$$
$$[\nu_{CO} = 1967\ cm^{-1}] \qquad [\nu_{CO} = 2075\ cm^{-1}]$$
$$(\epsilon\ 1150\ M^{-1}/cm^{-1}) \qquad (\epsilon\ 655\ M^{-1}cm^{-1})$$

Cl_2 with molecular specificity by using the infrared spectrum in the CO stretching region.[20] For both MoS_2 and $MoSe_2$, we find

that the photocurrent efficiency is >90% without correcting for Cl_2 that is lost by dissolving in the electrolyte solution. The current densities for which these current efficiencies were determined were ~10 mA/cm² for MoS_2 and ~45 mA/cm² for $MoSe_2$. These photocurrent densities were sustained for periods exceeding 50 h without obvious damage to the photoanode. In the ~45 mA/cm² $MoSe_2$ case, greater than 150 mol of Cl_2 were generated per mol of $MoSe_2$ without deterioration of the photoanode. Longer term tests of durability are now in progress. Experiments similar to those for Cl^- oxidation have been performed for Br^- oxidation. However, Br_2 remains in solution, and current efficiency was determined spectrophotometrically as compared to authentic Br_2 in 12 M LiBr. The initial current efficiency for n-type MoS_2 (10 mA/cm²) was >95% and for n-type $MoSe_2$ (70 mA/cm²) was >90%. Again, photocurrent can be sustained, and many turnovers based on the original number of moles of crystal can be obtained. It is particularly noteworthy that we find durability at electrode potentials significantly positive of the onset of photoanodic decomposition in 0.1–1.0 M supporting electrolyte (e.g., KCl, LiCl, LiBr, and $NaClO_4$).

The durability of MoS_2 and $MoSe_2$ photoanodes in aqueous 15 M LiCl or 12 M LiBr is the main finding. Generation of Cl_2 is the energetically most difficult oxidation process ever sustained in aqueous solution at a nonoxide photoanode. The durability is likely due to the super high X^- activity and the lower activity of H_2O that participates in the photocorrosion. Support for this conclusion comes from the fact that the onset for photoanodic corrosion moves more positive as the concentration of an "innocent" electrolyte $LiNO_3$ is increased; for example, at 0.1 M $LiNO_3$, the photoanodic current onset is at ~+0.2 V vs. SCE for MoS_2 while it is at ~+0.5 V vs. SCE at 10 M $LiNO_3$. In 10 M $LiNO_3$, the photocurrent efficiency at +0.7 V vs. SCE for 0.1 M Br^- oxidation (~30%) at illuminated MoS_2 is significantly higher than that for 0.1 M LiBr alone (~0% efficiency).[21] These data show an important role for both Li^+ concentration and high X^- concentration. Further details will be reported in the full paper.[22]

(15) When no X_2 is present, the evolution of H_2 occurs at the dark Pt cathode. Thus, the net chemistry is $X^- + H_2O \rightarrow \frac{1}{2}X_2 + \frac{1}{2}H_2 + OH^-$, when no X_2 is present at the cathode. Since the cathodic evolution of H_2 is a pH-dependent process, efficiencies are generally best given with reference to the half-cell reaction driven at the photoelectrode.

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Clifford P. Kubiak, Lynn F. Schneemeyer
Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

A General Preparative Method for α-Lithioethers and Its Application to a Concise, Practical Synthesis of Brevicomin

Sir:

Until recently, α-lithioethers were nearly always prepared by deprotonation of an α-carbon atom of an ether which has a special anion-stabilizing feature. Examples of the latter are substituents such as carbonyl,[1] cyano,[2] phenylthio,[3] or most commonly carbon–carbon unsaturation;[4] in addition, sp[2] hybridization of the ether carbon atom allows ready deprotonation by alkyllithiums even when anion-stabilizing substituents are absent.[5] Schöllkopf,[6] and later Peterson,[7] showed that α-lithiomethyl methyl ether can be prepared from α-stannylmethyl methyl ether precursors by exchange with an alkyllithium, and Still[8] has demonstrated how this principal can be applied to the preparation of α-lithioethers of types **1** and **2**, species which do not possess special anion-stabilizing features.

$$ROCH_2Li \qquad \underset{\displaystyle RCHLi}{\overset{\displaystyle OR'}{|}}$$

$$\mathbf{1} \qquad\qquad \mathbf{2}$$
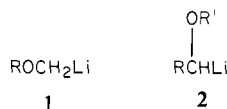
We now report that a variety of types of unstabilized and stabilized α-lithioethers can be rapidly prepared in tetrahydrofuran at –63 or –78 °C from α-(phenylthio)ethers by reductive lithiation

with lithium 1-(dimethylamino)naphthalenide (LDMAN)[9] or lithium naphthalenide (LN). What makes this method one of considerable generality is the ready availability of various types of α-(phenylthio)ether substrates or their vinylogues as demonstrated by eq 1–7.
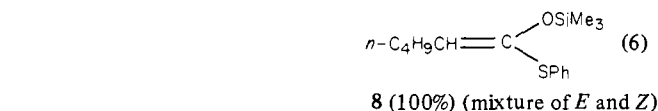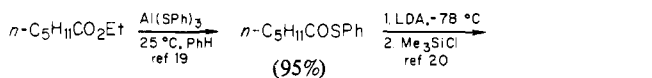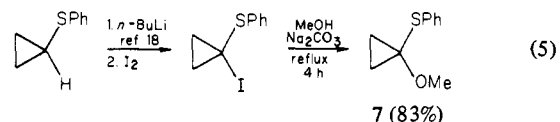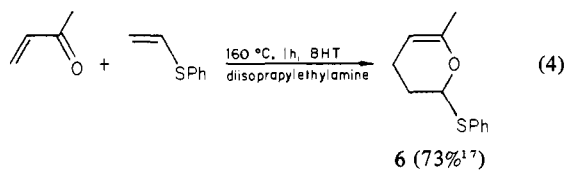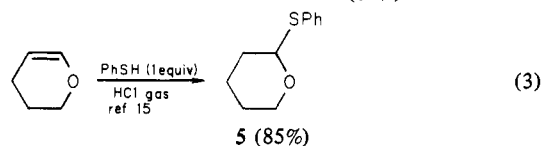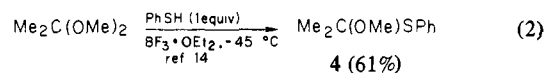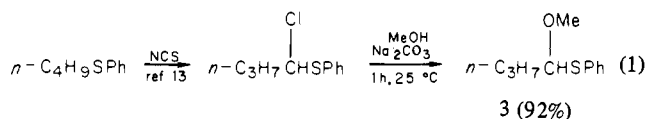
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