

ANGEWANDTE CHEMIE

Volume 30 · Number 7
July 1991
Pages 836-838

International Edition in English

Reprint

On the Electrochemical Oxidation of Cs[⊕] and Other Alkali-Metal Ions in Liquid Sulfur Dioxide and Acetonitrile**

By *Christophe Jehoulet* and *Allen J. Bard**

A recent paper suggested that Cs[⊕] (as the OTeF₅[⊖] salt) could be oxidized electrochemically at a Pt electrode in acetonitrile solutions containing Et₄N[⊕]PF₆[⊖] at ca. +3 V vs. SCE (near the background oxidation limit of MeCN).^[1] The addition of cryptand decreased the potential for the observed oxidation to 2.7 V vs. SCE. Similar oxidation waves were not seen with K[⊕], Rb[⊕], and *n*Bu₄N[⊕] salts of OTeF₅[⊖]. However, the oxidation of Cs[⊕] at such a relatively low potential appears to be at variance with our studies of electrochemical oxidations in liquid SO₂, which has been shown to have a background oxidation limit of > +5 V vs. SCE, considerably beyond that of MeCN.^[2-4] Indeed, in a recent

paper^[4] it was shown that a CsAsF₆ supporting electrolyte in liquid SO₂ allowed studies to +5 V without apparent oxidation of the Cs[⊕]. We report here cyclic voltammetric studies of Cs[⊕] and other alkali-metal ions in liquid SO₂ which suggest that oxidation of these ions may be possible, but only at considerably more positive potentials than those suggested from the MeCN studies.^[1] These studies were carried out with an ultramicroelectrode^[5] (UME) (10- or 25-μm diameter) to minimize effects of solution resistance and allow studies of the salts to be carried out in the absence of supporting electrolyte.^[3,4] The possibility of hydration of these salts and its influence on the electrochemical response was also examined. Finally, we reexamined the behavior of these compounds in MeCN.

Experiments in SO₂ with CsAsF₆ as a supporting electrolyte in the study of other compounds have been reported.^[4] However, we have not been able to reproduce some aspects of this earlier work. For example, we found the maximum solubility of CsAsF₆ at -70°C to be about 4 mM and oxidation of Cs[⊕] to occur at less positive potentials. Figure 1 A shows a cyclic voltammogram (CV) of a 4 mM solution at a 10-μm UME in SO₂ without added supporting electrolyte. Figure 1 A was obtained for a saturated solution; the solubility of CsAsF₆ and the other alkali salts in liquid SO₂ was very low (≈4 mM for CsAsF₆ and even lower for the other alkali-metal salts). The CV recorded with an UME (10-

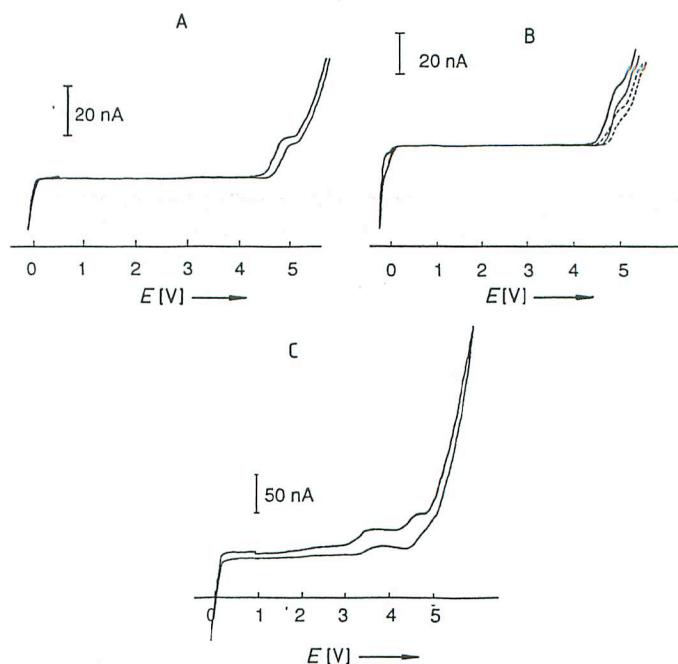


Fig. 1. Cyclic voltammogram of solutions of Cs[⊕] at 203 K in liquid SO₂. Scan rate, 1 Vs⁻¹; working electrode, platinum disk, 10-μm diameter (A and B), 50-μm diameter (C). A) Saturated solution of CsAsF₆ (≈4 mM) without supporting electrolyte. B) CsAsF₆ (3.5 mM) with *n*Bu₄NAsF₆ (5.2 mM). Solid curve: compound in presence of supporting electrolyte. Dashed curve: supporting electrolyte alone. C) Saturated solution of CsClO₄ without supporting electrolyte.

or 25-μm diameter) did not show a reverse cathodic wave, even for higher scan rates (up to 20 Vs⁻¹), suggesting low stability of the oxidation product. The half-wave potential *E*_{1/2}, was 4.75 V vs. SCE for CsAsF₆. The other alkali salts, KAsF₆ or RbAsF₆, were also studied in the absence of supporting electrolyte and displayed similar electrochemical behavior (*E*_{1/2} values of 4.64 and 4.66 V vs. SCE for K[⊕] and Rb[⊕], respectively). However, SO₂ is a resistive solvent and in order to get more quantitative information, it was necessary

[*] Prof. A. J. Bard, Dr. C. Jehoulet
Department of Chemistry, The University of Texas at Austin
Austin, TX 78712 (USA)

[**] Electrochemistry in Liquid SO₂, Part 10. This work was supported by the National Science Foundation (CHE8901450). Part 9: [4]

to compensate for the effect of ohmic drop and migration. Therefore, experiments were performed with $n\text{Bu}_4\text{NAsF}_6$ as a supporting electrolyte. We found this electrolyte to be oxidized at slightly more positive potentials than Cs^\oplus ($E_{1/2} = 4.9 \pm 0.1$ V vs. SCE). Electrolytes with shorter alkyl chains^[4] oxidize at more positive potentials, but their lower solubilities and rates of dissolution made them less convenient than $n\text{Bu}_4\text{NAsF}_6$. A CV for the oxidation of Cs^\oplus is shown in Figure 1B. The oxidation wave did not display a reverse wave and occurred at about the same potential as that for the oxidation of $n\text{Bu}_4\text{N}^\oplus$, as expected from the $E_{1/2}$ values of the alkali salts found in the preliminary experiments. The other alkali salts displayed the same electrochemical behavior.

The $E_{1/2}$ values for the oxidation of various alkali cations are given in Table 1. These correspond to those found for the experiments without supporting electrolyte. The $E_{1/2}$ found

Table 1. Electrochemical parameters of alkali salts.

| Salt | $E_{1/2}$ [V] vs SCE | D [$10^{-5} \text{cm}^2 \text{s}^{-1}$] | | d [\AA] [a] | | r [\AA] [9] |
|--------------------|-------------------------|---|---------|--------------------------|---------|--------------------------|
| | | $n = 1$ | $n = 2$ | $n = 1$ | $n = 2$ | |
| CsAsF ₆ | 4.73 ± 0.07 | 1.68 | 0.84 | 5.9 | 11 | 1.65 |
| RbAsF ₆ | 4.67 ± 0.07 | 2.10 | 1.05 | 4.75 | 9.5 | 1.49 |
| KAsF ₆ | 4.64 ± 0.1 | 2.38 | 1.19 | 4.1 | 8 | 1.33 |
| NaPF ₆ | 4.8 | — | — | — | — | — |

[a] Calculated from the Stokes–Einstein relationship.

for Cs^\oplus is much more positive than the one reported previously.^[11] The experiments were also conducted as a function of salt concentration. The limiting current (i_l) varied with concentration (Fig. 2), in the absence and presence of supporting electrolyte. The linear variation observed shows that the oxidation wave is effectively due to the oxidation of the added salt. Unfortunately, we could not determine the number of electrons, n , involved in the electrode reaction by coulometry. However, a rough estimate of the diffusion coefficient, D , was made assuming a one- or a two-electron charge-transfer reaction and using the expression of the steady-state current for a micro-disk.^[15] The values obtained at -70°C are given in Table 1. Those values can be used together with the Stokes–Einstein equation to estimate the diameter of the solvated ion. The values obtained in the case

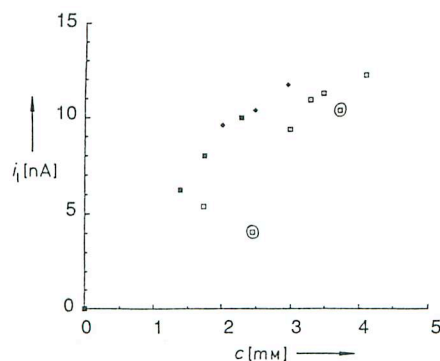


Fig. 2. Steady-state current as a function of concentration for various salts. \blacklozenge = RbAsF_6 ; \blacksquare = KAsF_6 ; \square = CsAsF_6 . Circled values were recorded without supporting electrolyte; these currents are lower because of electrorepulsion (migration) effects on the cation at these very positive potentials. The current was determined after subtraction of the $n\text{Bu}_4\text{N}^\oplus$ background. The reduction of the solvent was chosen as a reference potential. This procedure does not allow the use of a large amount of supporting electrolyte (1–10 mM) and therefore requires measurement with UMEs. (Working electrode: platinum disk, 10- μm diameter).

of a one-electron transfer seem more compatible with the value of the crystalline radius, even in the case of solvation by molecules of solvent.

Several other experiments were undertaken to demonstrate that the oxidation was due to the alkali-metal ion rather than the anion (AsF_6^\ominus) or adventitious water. For example, alkali-metal salts are easily hydrated and this can affect their electrochemical behavior. Therefore, alkali salts were dried in a vacuum oven at 150°C for 48 h and stored in a dry box under a helium atmosphere. To determine the amount of water in the compounds and its possible effect on the voltammograms, the salts were titrated by the Karl Fischer method. The reagent (Fluka) was standardized with sodium tartrate dihydrate salt as described by Neuss et al.^[6] Titrations were performed with both visual and amperometric end-point detection. To prevent any contamination of the reagents, titrations were conducted^[7] in the dry box under a helium atmosphere. All reagents were opened and used only in the dry box. This should exclude all contamination by external moisture.

After the standardization of the reagent, the salts were added in MeOH solution. There was no change in the color of the solution or in the amperometric current, even after stirring for more than 30 min. Thus, the water in the salt was less than 0.05%. This implies that, in each experiment, the concentration of water in the cell from the compound was less than $10 \mu\text{M}$. This low concentration is not compatible with the waves seen in the voltammograms. Moreover, when water was intentionally added to the solutions to observe its effect on the electrochemical behavior, it catalyzed the limiting oxidation process and produced sharp peaks totally different from the waves attributed to the alkali metals; the same behavior was observed with imperfectly dried compound. Sometimes the compounds also displayed a small wave at about 3.8 V vs. SCE, which can be assigned to the moisture from the salt. This wave was also observed when a small amount of water was added to the solution. These observations suggest that the alkali-metal wave in the voltammograms cannot be attributed to free water or that bound to ions.

Finally, to demonstrate that the wave was not due to AsF_6^\ominus oxidation, CsClO_4 was examined in SO_2 in the absence of supporting electrolyte. The voltammogram (Fig. 1C) displayed two oxidation waves. The first one is assigned to the oxidation of the perchlorate anion, as observed in previous studies.^[2, 8] The other $E_{1/2}$ was the same as that observed with CsAsF_6 solutions.

This study suggests that the alkali-metal cations might be oxidized, but only at high potentials in SO_2 . This oxidation cannot be observed in MeCN. The electrochemical behavior of CsAsF_6 in MeCN was studied in our laboratory and Fig-

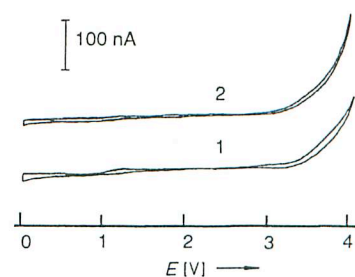


Fig. 3. Cyclic voltammograms of CsAsF_6 in acetonitrile at 298 K. 1) $n\text{Bu}_4\text{NPF}_6$ (0.1 M) and [2.2.2]cryptand (5.9 mM) in acetonitrile. 2) In the presence of CsAsF_6 (6 mM). Acetonitrile was dried on Woelm neutral activated alumina before use. Scan rate, 0.2Vs^{-1} ; working electrode, platinum disk, 25 μm diameter.

ure 3 shows that the voltammogram does not display any oxidation wave before background, even in the presence of cryptand, introduced to stabilize the oxidized form of the alkali cation.

The oxidation of Cs^\oplus and the other alkali-metal ions in SO_2 is not unambiguous. It is surprising that Cs^\oplus , Na^\oplus , and K^\oplus are oxidized at the same potential, given their very different ionization potentials in the gas phase. However, salts from different origins show the same behavior, suggesting that a common impurity is unlikely. Water, the most likely candidate impurity, does not show this CV behavior, and the effect of added electrolyte suggests the oxidation wave can be attributed to a positive species.

Experimental Procedure

The measurements, the purification of SO_2 , and the preparation of the supporting electrolyte, $n\text{Bu}_4\text{NAsF}_6$ and the alkali salts (CsAsF_6 , RbAsF_6 , KAsF_6) followed the procedure described previously [3, 4]. NaPF_6 (Aldrich) was used after recrystallization from $\text{Me}_2\text{SO}/\text{CH}_2\text{Cl}_2$ and drying in a vacuum oven under the same conditions as above.

Experiments in MeCN were performed in a dry box (Vacuum Atmospheres) under a helium atmosphere using high-purity MeCN with a low concentration of water (0.003%) (Burdick & Jackson). Kryptofix (Aldrich) and Woelm neutral activated alumina (ICN Biomedicals) were used as received. The supporting electrolyte, $n\text{Bu}_4\text{NPF}_6$, was thrice recrystallized from EtOH/THF (1:1), then dried in a vacuum oven and stored in the dry box.

Received: December 11, 1990 [Z 4318 IE]
German version: *Angew. Chem.* 103 (1991) 882

- [1] K. Moock, K. Seppelt, *Angew. Chem.* 101 (1989) 1713; *Angew. Chem. Int. Ed. Engl.* 28 (1989) 1676.
- [2] L. A. Tinker, A. J. Bard, *J. Am. Chem. Soc.* 101 (1979) 2316.
- [3] E. Garcia, J. Kwak, A. J. Bard, *Inorg. Chem.* 27 (1988) 4377.
- [4] E. Garcia, A. J. Bard, *J. Electrochem. Soc.* 137 (1990) 2752.
- [5] R. M. Wightman, D. O. Wipf in A. J. Bard (Ed.): *Electroanalytical Chemistry*, Dekker, New York 1989, p. 267, and references cited therein.
- [6] J. D. Neuss, M. G. O'Brien, H. A. Frediani, *Anal. Chem.* 23 (1951) 1332.
- [7] J. Mitchell, Jr., D. M. Smith: *Aquametry*, Vol. 3, Wiley, New York 1980.
- [8] P. Castellonese, G. Launay, *Bull. Soc. Chim. Fr.* 7-8 (1978) I-317.
- [9] L. Pauling: *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, USA 1960; *Die Natur der chemischen Bindung*, Verlag Chemie, Weinheim 1976.