

**Cross Sections for the formation of Negative Ions by Electron Impact on
OCS**

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ABSTRACT

Cross sections, appearance energies and energies at which negative ion intensities are maximum (peak energy) have been measured for electron attachment to OCS as a function of electron impact energy in the energy range of 0 to 20 eV. Ions of S⁻, O⁻, and C⁻ are formed through the dissociative attachment process. It is found that S⁻ is formed at four peak energies of 1.4, 4.7, 7.0, and 10.2 eV. Among these the formation at 1.4 eV is the strongest, being almost 200 times greater than the others. Ion intensities of O⁻ and C⁻ are weak, resulting in greater uncertainty in the measured cross sections. By using thermochemical data we have identified various channels of dissociation. Cross sections for the formation of C⁻ have been measured for the first time.

1. Introduction

Formation of negative ions by **electron** attachment to **carbonyl** sulfide (OCS) has been studied in the past by **Dillard** and **Franklin** (1968), **MacNeil** and **Thynne** (1969), **Ziesel** et al (1975), **Hubin-Franskin** et al (1976), **Abouf** and **Fiquet-Fayard** (1976), and **Tronc** et al (1982). Although these investigations have provided information regarding the ionic species formed, their peak energies (i.e. the electron impact energy at which the negative ion formation intensity is maximum), probable mechanisms of formation and relative ion intensity ratios, the data are fragmentary and in some cases show inconsistencies. Among the **species** formed, as a result of electron attachment to OCS, S^- was studied extensively. The investigations of **Ziesel** et al (1975), **Abouf** and **Fiquet-Fayard** (1976), and **Tronc** et al (1982) were carried out for incident electron energies from 0 to 2.2 eV. In this energy range a strong peak with maximum around 1.35 eV was seen and was assigned to a dissociative attachment channel ($e^- + OCS \rightarrow CO + S^-$) associated with the lowest **shape resonance** of the ground state of OCS. It was also found that the resulting CO fragment was formed in its ground electronic state at various vibrational levels. Absolute values of cross sections for the formation of S^- were measured only by **Zeisel** et al (1975) for the negative ion peak centered at 1.4 eV. Two additional **resonance features** for S^- with peak energies at about 7.5 eV and 11 eV were also reported by **MacNeil** and **Thynne** (1969). These were not observed in the more **recent** work of **Hubin-Franskin** et al (1975). On the other hand, several spectral **features** related to O^- formation from OCS with maxima at 4.2, 7.2, 8.1, 9.6, 11.0, and 11.4 eV, reported by **Hubin-Franskin** et al (1975), were not found by **MacNeil** and **Thynne** (1969). Instead, they reported only two spectral features with peaks at 5.2 and 8.9 eV. They **further** reported the formation of C^- at 50 eV

electron impact energy and concluded that these species were not formed at lower electron impact energies.

Thus, in summary, only the S^- ions resulting from the dissociative attachment at electron impact energy of 1.4 eV, were studied in detail. The cross section values for this process has been reported by only one group, Although S^- ions were detected at high electron impact energies the published data seem to be unreliable. Cross sections for the generation of C^- and O^- ions from **OCS** are not readily available.

In view of the above disagreements among various data we **carried** out measurements on **OCS** and obtained normalized values of cross sections for the formation of S^- and C^- ions produced by electron attachment. Due to serious background contribution of O^- from **H₂O**, reliable data for O^- from **OCS** could not be obtained. Therefore, the cross section data for O^- are not reported here. In section 2 we **will** briefly present the experimental method and the data reduction technique and in section 3 the results will be discussed and compared with previous measurements.

2. Experimental apparatus and method

The experimental apparatus and method of data reduction have been described in detail elsewhere (Rao and Srivastava, 1993). Therefore, only a brief description will be given here. A schematic diagram of the apparatus is shown in figure 1. It consists of a pulsed electron gun which produces pulsed beam of energy-selected electrons with a pulse width of about 100 ns and an energy resolution of about 0.5 eV. The electron beam is collimated by a magnetic field of about 100 G which is produced by a solenoid. This beam crosses at 90° a molecular beam which is generated by flowing the gas under study through a capillary array. The ions produced in the interaction volume are extracted by a pair of extraction grids (see figure 1) and transported to a charged-particle detector by a time-of-mass spectrometer (TOFMS, Srivastava et al, 1995)

The negative ions formed by the interaction of electrons with OCS were mass and energy analyzed by the TOFMS. The intensity of each selected ion was recorded by a multichannel scalar (MCS) as a function of electron impact energy. These recorded data represent the relative values of cross sections of the various ionic species at different electron impact energies. These relative values of cross sections obtained for S⁻ and C⁻ ions were then normalized by utilizing the relative flow technique (Krishnakumar and Srivastava, 1988). For this normalization, the cross section values for O⁻ production from CO₂ by dissociative electron attachment at 4.4 and 8.2 eV were employed (Orient and Srivastava, 1983). These peak energies were in turn used for calibration of electron energy scale.

The TOFMS combined with the ion extraction system was calibrated to obtain the efficiency of mass-to-charge transmission of the apparatus by utilizing the rare gas atoms in the positive ion mode of operation (Rao and Srivastava, 1993). For the detection of

negative ions the polarities of **all** voltages were reversed. We estimate the error in the values of cross sections to be about 1 *So*0. Details on the error analysis can be found in a publication by **Krishnakumar** and **Srivastava** (1 988).

The appearance energy (A. E.) of each **feature** was obtained by extrapolating the rising slope of the resonance feature until it crossed the constant background. It was estimated that the A. E.'s obtained this way are accurate to within ± 0.25 eV (**Rao** and **Srivastava**, 1993).

3. Results and discussion

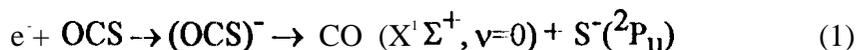
The negative *ion* spectra resulting from the dissociative attachment of electrons with OCS showed the presence of three ions S⁻, C⁻ and O⁻. However, no measurements were made for O⁻ production because of its extremely weak signal. Figures 2 and 3 show normalized values of cross sections for S⁻ and C⁻ ions, respectively, as a **function** of electron impact energy. Figure 4 presents time-of-flight **spectra** for S⁻ ions formed at 4 different attachment energies (i.e. S⁻ ions corresponding to **features** a, b, c, and d of figure 2). In the following our results will be presented and discussed in **detail** for each ionic species:

S⁻ formation: Cross sections for the formation of S⁻ were measured for the electron impact energy range of 0 to 20 eV and are shown in figure 2. Four dissociative attachment **features** were observed at 1.4, 4.7, **7.0 and 10.2** eV. Previous investigations (**Dillard** and **Franklin**, 1973; **MacNeil** and **Thynne**, 1969; **Ziesel** et al., 1975; **Hubin-Franskin** et al 1976) reported the presence of the **feature** at 1.4 eV only. However, the present measurements revealed three additional features. Appearance energies (A.E) and Peak energies (P.E) for these resonant processes are given in table 1 along with the previously published data. In

this table we also present probable mechanisms for the dissociative attachment processes leading to S⁻ formation.

The spectral feature at 1.4 eV is the strongest and its intensity is almost two orders of magnitude larger than others (see figure 2). The present peak energy of 1.4 eV agrees well with the previously reported values of Hubin-Franskin et al. (1976) and Ziesel et al. (1975). However, the values of Dillard and Franklin (1968) and MacNeil and Thynne (1969) are about 0.8 eV higher. The only previously reported peak cross section value, $2.9 \times 10^{-17} \text{ cm}^2$, by Ziesel et al (1975) is in excellent agreement with the present value $2.6 \times 10^{-17} \text{ cm}^2$. The energy balance analysis (Ziesel et al. 1975) for the feature at 1.4 eV indicates that S⁻(²P_u) and CO (X¹X⁺) are formed as a result of dissociative attachment. The A. E. and P. E. for this feature suggest that, in fact, it corresponds to a short lived 211 resonance predicted by Lynch et al. (1979) in their elastic electron scattering calculation and observed in the differential (Sohn et al. 1987) and total (Szmytkowski 1983) scattering cross sections for e⁻ + OCS collisions.

Thus, the dissociative attachment process for the formation of S⁻ can be represented by the following equation:



The thermochemical threshold, 1.08 eV, for this process was calculated by employing the values of bond dissociation energy (Darwent, 1970) and electron affinity of sulfur (Lineberger and Woodward 1970). The A. E., as measured by us, is $0.5 \pm 0.25 \text{ eV}$ which is much lower than the predicted thermochemical threshold, which indicates that S⁻ ions and CO are formed with thermal energies.

The resonance **features** b, c, and d **shown** in figure 2 at peak energies of 4.7, 7.0 and 10.2 eV, respectively, are weak. The results of MacNeil and Thynne (1969) show two **features** at 7.4 and 10.8 eV which may be the same as the last two in our spectra. However, none of the earlier studies reported any **feature** in the 4 to 5 eV energy range. In e⁻ - OCS scattering experiments a weak resonance at 4.1 eV was observed in the total cross section measurements (Szmytkowski, 1983). Sohn et al. (1987) have also reported a weak structure at about 3.2 eV in the energy dependent elastic differential cross section at 130° scattering **angle**, which was identified as a d-wave resonance (2A). In addition, their integrated elastic cross sections show a maxima at about 4 eV. Thus, we believe that the S⁻ feature at 4.7 eV is probably due to the 2_A shape resonance of the ground state of OCS. The appearance energy of this **feature** measured by us is 3.9 eV. The energy balance analysis shows that only the ground state of CO can be formed because the first electronic excited state of CO is at 6.3 eV (Krupenie, 1966). The excess energy will be distributed among the fragments (i.e. CO (X¹Σ⁺), S⁻(²P_u)) in the form of translational and **ro-vibrational** energies. In figure 4 one can see that S⁻ for the 4.7 eV **feature** is, in fact, faster than the S⁻ resulting from the dissociation process related to 1.4 eV feature.

The lack of spectroscopic information in the literature on the molecular states of OCS makes the assignment of 7.0 eV **feature** difficult. However, a close look at the total cross sections for e⁻ - OCS scattering (Szmytkowski, 1983) shows the existence of a very weak structure at about 7.0 eV. This resonance was not predicted in the multiple-scattering elastic calculation (Lynch et al. 1979). We tentatively assume that S⁻ (feature C) centered at 7.0 eV is generated through a **dissociative channel** via a resonance associated with a low lying excited state of OCS. The appearance energy for this process is 6.00.3 eV (see table 1). The energy balance analysis for this **feature** shows that the dissociation products are S⁻(²P_u) and CO (X¹Σ⁺) and an excess energy of about 6 eV is distributed between

the two fragments. This is evident from figure 4 where the TOF spectrum reveals that indeed the S related to 7.0 eV feature is faster than those related to 1.4 eV and 4.7 eV.

The S feature associated with the dissociative attachment process centered at 10.2 eV (shown in figure 2) is broad and is about 2 times broader than the others. It indicates that this feature either results from short lived excited states of OCS or from the ground state of OCS with CO formation in the electronically excited state via one of the probable pathways shown in table 1.

We associate the spectral feature at 10.2 eV (figure 2) with the process 2(a) because only via this process can an excess energy of 3 eV result, which is similar to the 2_A resonance process related to 4.7 eV feature of figure 2. The TOF spectrum (shown in figure 4) for the S-, resulting from this process, supports this conclusion because the kinetic energy of S is about the same as for the feature at 4.7 eV.

C⁻ formation: Cross sections for C⁻ formation are shown in figure 3. As it is evident from this figure the cross sections are very small and arc, therefore, subject to large errors. Present measurements for the formation of C⁻ are the first ones. We distinctly see (shown in figure 3) three spectral features with peak energy positions at 1.3, 8.1 and 11.2 eV, and their respective appearance energies are given in table 2. Probably the lowest peak is related to 211 shape resonance which gives rise to a strong S⁻ signal. However, the thermochemical threshold for the process, C⁻ + SO, is about 7.6 eV. Therefore, the peak at 1.3 eV is difficult to explain. We would like to emphasize that the presence of this peak was verified by several measurements in our laboratory and under various experimental conditions. Our measurements are made under single collision conditions. Therefore, the production of C⁻ via ion-molecule reactions is to be ruled out.

4. Conclusions

Our measurements show that only three negative ions (i.e. C⁻, O⁻, and S⁻) are formed as a result of dissociative attachment of electrons with OCS for the electron **impact** energy range of 0 to 20 eV. Previous measurements were mainly **confined** to the detection of S⁻ at 1.4 eV electron attachment energy. There are other dissociative channels for the formation of S⁻ at higher electron impact energies. At low energy (≈ 1.3 eV) C⁻ is formed which cannot be explained on the basis of thermochemical considerations.

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References

- About R and Fiquet-Fayard F 1976 *J. Phys. B: At. Mol. Phys.* **9** L323
- Claizy P 1991 *Nature* **349**393
- Dillard J G and Franklin J L 1968 *J. Chem. Phys.* **48**2349
- Darwent B B 1970 "Bond dissociation energies in simple molecules", *Natl. Std. Ref. Data Ser., Natl. Bur. Stds. (U. S. GPO, Washington, DC)*
- Hubin-Franskin J, Katihawa J and Collin J E 1976 *Int. J. Mass Spectrom. Ion Phys.* **20** 2,85
- Krishnakumar E and Srivastava S K 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21**1055
- Krupenie P H 1966, "The Band Spectrum of Carbon Monoxide", *Natl. Std. Ref. Data Ser., Natl. Bur. Stds. (U. S.)* **5**
- Lineberger W C and Woodward B W 1970 *Phys. Rev. Lett.* **25**, 424
- Lynch M G, Dill D, Liegel J and Dehmer J L 1979 *J. Chem. Phys.* **71**4249
- MacNeil K A G and Thynne J C J 1969 *J. Phys. Chem.* **73**2960
- Orient O J and Srivastava S K 1983 *Chem. Phys. Lett.* **96**681
- Rao M V V S and Srivastava S K 1993 *J. Geophys. Res.* **98**13137-13145
- Schulz G J 1973 *Rev. Mod. Phys.* **45**273
- Sohn W, Kochem K H, Schuerlein K M, Jung K and Ehrhardt J 1987 *J. Phys. B: At. Mol. Opt. Phys.* **20**3217
- Srivastava S K, Tga I and Rao M V V S 1995 *Meas. Sci. Technol.* **6**1-4
- Szmytkowski C 1983, *XII Int. Conf. on the Physics of Electronic and Atomic Collisions*, Berlin, (Amsterdam, North-Holland), p 242
- Tronc M, Malegat L and Azria R 1982 *Chem. Phys. Lett.* **92**551
- Ziesel J P, Schulz G J and Milhaud J 1975 *J. Chem. Phys.* **62**1936

Table 1

Appearance energies (A. E.) and energies at the peak (peak energy) of cross sections curves in eV, for the formation of S from COS.

Features **a**, **b**, **c**, and **d** are shown in Fig. 2.

Appearance Energy (A. E.) (eV)					Peak Energy (P. E.) (eV)					Probable Pathways
(i)	(ii)	(iii)	(iv)	this work	(i)	(ii)	(iii)	(iv)	this work	
1.3	1.07	1.2	1.05	0.4	2.05	1.35	2.07	1.4	1.4 (feature a)	CO (X $^1\Sigma^+$) + S $^-$ (2P_u)
—	—	--	--	3.9	—	—	--	--	4.7 (feature b)	"
6.7	—	—	—	6.0	7.4	—	—	—	7.0 (feature c)	"
9.2	—	—	—	8.2	10.8	—	—	—	10.2 (feature d)	2(a) CO (a $^3\Pi$) + S $^-$ (2P_u) 2(b) CO (a' $^3\Sigma$) + S(2 ?.) 2(c) CO (d $^3\Delta$) + S $^-$ (2P_u) 2(d) CO(D $^1\Delta$) + S $^-$ (2P_u)

(i) MacNeil and Thynne[1969]

(iii) Dillard and Franklin [1968]

(ii) Ziesel et. al. [1975]

(iv) Hubin - Franskin et. al. [1976]

Table 2

Appearance energies (A. E.) and energies at the peak (peak energy) of cross sections curves in eV for the formation of C from COS.

<u>Appearance Energy (A.E.) (eV)</u>	<u>Peak Energy (P.E.) (eV)</u>	<u>Probable Pathways</u>
this work	this work	
0.4	1.3 (feature a)	
7.4	8.1 (feature b)	c-A SO
9.6	11.2 (feature c)	v

Figure Captions:

Figure 1. A Schematic diagram of the experimental apparatus.

Figure 2. S^- production resulting from dissociative electron attachment to OCS. ● , Ziesel et al. (1975); solid line, present results. See text for details on features a, b, c and d; e is the onset of polar dissociation.

Figure 3. C^- production resulting from dissociative electron attachment to OCS.

Figure 4. Time-of-flight spectra of S^- for the **features** a, b, c, and d shown in figure 2.

