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H. Okabe, A. H. Laufer, and J. J. Ball

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Photodissociation of OCCl₂ in the Vacuum Ultraviolet: Production and Electronic Energy of Excited Cl₂

H. OKABE, A. H. LAUFER, AND J. J. BALL National Bureau of Standards, Washington, D. C. 20234 (Received 8 February 1971)

The photodissociation of OCCl₂ in the vacuum ultraviolet yields electronically excited Cl₂ producing emission continua in the region 2000–3100 Å. A curve obtained by plotting fluorescence efficiencies as a function of incident wavelength shows diffuse vibrational structure corresponding to the ν_1 symmetric stretching mode of OCCl₂, indicating that the process is predissociative. Three main continua at 3063, 2565, and 2460 Å were observed by the photolysis of OCCl₂ with the Kr 1236-Å line, while only one continuum at 2580 Å was obtained by the Xe 1470-Å line. From threshold energies of the incident photons to produce each continuum it was possible to obtain electronic energies of excited Cl₂. Electronic energies thus obtained are 7.21 ± 0.05 eV and 7.93 ± 0.03 eV for the upper state associated with the 2580- and 3063-Å continua, respectively. The electronic energy of the upper state responsible for the 2460-Å continuum lies between 7.33 and 8.93 eV. The effect of inert gas on the emission continua was investigated. A comparison has been made of the emission continua obtained by the photolysis of OCCl₂ has been measured in the region 1170–1600 Å.

INTRODUCTION

It has been generally accepted^{1,2} that the primary photochemical process of $OCCl_2$ in the near ultraviolet is the production of Cl by Reaction (1):

$$h\nu$$

OCCl₂ \rightarrow CO+2Cl, $\Delta H = 3.56$ eV. (1)

In the vacuum-ultraviolet photolysis of OCCl₂, Dyne and Style³ reported the production of an emission continuum at about 2500 Å. Since similar emission continua were observed from Cl₂ excited by a high-frequency electrical discharge⁴ and also by active nitrogen,⁵ they concluded that the photolysis of OCCl₂ produced electronically excited Cl₂(Cl₂*),

$$\underset{\text{OCCl}_2 \to \text{CO} + \text{Cl}_2^*}{\overset{h\nu}{\longrightarrow}}$$
(2)

An analogous reaction (3), the production of the ground state Cl_2 , has apparently not been reported,

$$h\nu$$

OCCl₂ \rightarrow CO+Cl₂, $\Delta H = 1.07$ eV. (3)

Cameron and Elliott⁵ attributed the 2580 Å continuum to the transition from a stable upper state located above 6.5 eV to a lower state whose potential-energy curve has a shallow minimum. The reaction of OCCl. with metastable Ar resulted in the production of 2580and 3063-Å Cl₂ emission continua as well as CO $a^{3}\pi$.⁶ The purpose of this work is to investigate Reaction (2), the photolytic production of Cl2*, in more detail to find the nature of the process and to obtain electronic energies of various excited Cl₂ which do not appear to have been determined. The fluorescence efficiencies measured as a function of incident wavelength should indicate whether the process is predissociative, and threshold energies of the incident photons for the production of Cl2* should give information on the electronic energies of Cl₂*.

EXPERIMENTAL

The detailed description of the apparatus has already been given.^{7,8} The emission spectra produced from photodissociation of OCCl₂ by the Kr (1236, 1165 Å) and by the Xe (1470, 1295 Å) resonance lamps were observed by means of a 13-stage photomultiplier attached behind the exit slit of a 1-m normal incidence vacuum-ultraviolet monochromator with a 600-lines/ mm grating.

A hydrogen discharge lamp located in front of the entrance slit of the same monochromator served as a light source for measuring the absorption coefficient and the fluorescence efficiencies produced from photodissociation of OCCl₂. The intensity of the fluorescence, I_f , was measured at right angles to the incident beam with a 13-stage photomultiplier having an Sb-K-Cs (bialkali) photocathode. The fluorescence efficiencies, I_f/I_0 , where I_0 , the intensity of the incident beam measured by another 13-stage photomultiplier coated with sodium salicylate, were obtained as a function of incident wavelength. For the measurement of the sum of the 3063- and 2580-Å emission intensities from photolysis of OCCl₂, an appropriate glass filter transmitting light of wavelength between 2300 and 4200 Å was inserted in front of the photomultiplier. For the 3063 Å continuum an interference filter which has a maximum transmission of 27% at 3100 Å and a bandwidth of 100 Å at half-maximum replaced the glass filter. The pressure of a sample below 5 torr was measured by a calibrated diaphragm gauge and above 5 torr by a calibrated mechanical gauge. In order to purify OCCl₂, the bulk of the sample obtained commercially was collected in a trap kept at -105° C and CO₂ present in the sample in large quantities passed on to a second trap cooled by liquid nitrogen. The fractionation was repeated several times. A mass spectrometric analysis showed that the purified sample contained 15% CO₂ as the only impurity. The absorption coefficient of OCCl2 was corrected accordingly. N2 and Ar,



FIG. 1. Absorption coefficient k of OCCl₂ in the region 1400-1600 Å where k is defined as $I = I_0 e^{-k_p l}$ (see text). Points were taken at 1-Å interval; pressure, 0.1-0.4 torr; cell length, 6.95 cm; resolution, 0.8 Å. For designations see Ref. 9. σ (cm²) = 4.06×10⁻²⁰ k(atm⁻¹·cm⁻¹).

obtained commercially, were used without further purification. Cl_2 , obtained commercially, was of research grade and was used without further purification.

RESULTS

Absorption Coefficient of OCCl₂

The absorption coefficient of OCCl₂ was measured with a slitwidth of 50 μ m, corresponding to a 0.8 Å bandwidth. The pressure was varied between 0.1 and 0.4 torr, depending on the extent of absorption. The points were taken at 1 Å intervals in the region 1170– 1600 Å, and the results are presented in Figs. 1 and 2.

The absorption coefficient, k, is defined as $I = I_0 \exp(-kpl)$, where I_0 and I are the intensities of the incident and transmitted light, respectively, p, pressures in atmospheres, and l, cell length in centimeters (in this case, 6.95 ± 0.01 cm). The absorption spectrum of OCCl₂ has been measured by LaPaglia and Duncan⁹ in the region 600-2000 Å. In accordance with their observation, five electronic transitions were found in the region 1170-1600 Å, which are designated from I-V in Figs. 1 and 2, according to LaPaglia and Duncan.

Transition I is a broad continuum with a maximum at about 1540 Å and k of 2000 $(atm \cdot cm)^{-1}$. Transition II contains 16 vibrational bands of the ν_3 mode (symmetric Cl bending). Transition III consists of six comparatively sharp bands of the ν_3 mode. Transition IV has six diffuse features of the ν_1 type (symmetric stretching) followed by a region of strongest absorption, V. Apparently none of these transitions belongs to a Rydberg series.⁹

Emission Continua from Photodissociation of OCCl₂

Figure 3(a) shows the emission continua observed when 0.2 torr of OCCl₂ was irradiated by the Kr (1236-, 1165-Å) lines (full line). The spectrum was scanned at a speed of 100 Å per minute with a time constant of 1 sec. A slitwidth used was 0.2 mm, corresponding to a 3-Å bandwidth. The spectrum appears continuous with three main maxima at 3065, 2565, and at about 2460 Å. The positions of the maxima and the contour coincide well with those of Cl₂ excited by a high-frequency electric discharge,⁴ although in the electric discharge the first and the third maxima are much more intense. The third maximum (2460 Å) in the Kr



F1G. 2. Absorption coefficient OCCl₂ in the region 1170–1400 Å.

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excitation is located at a longer wavelength than that in the discharge (2432 Å), probably because of the influence of the intense maximum at 2565 Å. Addition of N₂ and Ar were found to have a marked effect on the appearance of the emission continua. The dashed line in Fig. 3(a) shows the effect of 30 torr N_2 added to 0.2 torr OCCl₂. The major changes observed were: (1) the 3063- and 2460-Å continua were depressed almost entirely, while (2) the maximum of the 2565-Å continuum shifted to 2580 Å with an increase of its intensity by more than a factor of 2; (3) the continuum contained many diffuse bands. The appearance of the continuum is very much similar to that observed by Cameron and Elliott⁵ when Cl₂ is excited by active nitrogen. The same effect was observed when 100 torr of Ar was added to 0.2 torr $OCCl_2$. Figure 3(b) shows the emission spectrum taken when 0.2 torr $OCCl_2$ is



FIG. 3. (a) Full line: emission continua observed from 0.2 torr $OCCl_2$ excited by the Kr lamp. The spectrum was scanned with a speed of 100 Å per minute and a time constant of 1 sec. Resolution, 3 Å. Dashed line: emission spectrum when 30 torr N₂ was added to the above sample. (b) Solid line: emission continuum from 0.2 torr $OCCl_2$ excited by the Xe lamp. Scanning speed, 100 Å per minute; time constant, 1 sec; resolution, 6 Å. Dashed line: emission spectrum with 60 torr of Ar added to the sample.

excited by the Xe (1470-, 1295-Å) lines (full line). Since the emission intensity was much weaker than that produced by the Kr lines a slitwidth of 0.4 mm, corresponding to a 6-Å bandwidth, had to be used. The spectrum consists almost entirely of the 2580-Å continuum. When 60 torr of Ar are added to 0.2 torr of OCCl₂, the maximum increases by about 40% with an appearance of some diffuse bands (dashed line).

In addition the following observations were made:

(1) No other emission band or continuum was observed in the region 1800–6000 Å upon photolysis of $OCCl_2$ by the Kr lines.

(2) The same emission continua were observed either in a flow or a static system from photolysis of $OCCl_2$ by the Kr lines.

(3) When 0.4 torr Cl₂ was irradiated by the Xe lines, emission continua appeared at 3063 and 2565 Å with almost equal intensity. There was also an intense emission below 2000 Å. No emission in the region 1700– 6000 Å was observed when 3 torr of Cl₂ was excited by light in the wavelength region 1500–2000 Å.

(4) In the 1470-Å (Xe lamp with BaF_2 window) photolysis of OCCl₂, only the 2580-Å continuum was found.

(5) The same emission continua were observed from OCCl₂ by the 1236-Å excitation (Kr lamp with CaF₂ window) as well as the 1236- and 1165-Å excitation (Kr lamp with LiF window), although the intensity ratio of the 2565-Å continuum to the 3063-Å continuum was much larger in the latter excitation.

(6) The intensities of the 3063-Å continuum relative to the 2565 Å from $OCCl_2$ photolysis were measured as a function of incident wavelength. They were 0.03, 0.10, 0.20, and 0.22 at 1350, 1300, 1250, and 1215 Å, respectively.

Fluorescence Efficiency from OCCl₂ Photolysis

The fluorescence efficiencies for the 3063- and 2580-Å continua were obtained as a function of incident wavelength with a slitwidth of 0.2 mm (corresponding to a 3-Å bandwidth) at a scanning speed of 10 Å per minute and a time constant of 5 sec. For the weak 3063-Å continuum a slitwidth of 0.5 mm, corresponding to a bandwidth of about 8 Å, had to be used with the same scanning speed. Figure 4 shows the fluorescence efficiency curve in the region of incident wavelength from 1170–1560 Å when 0.11 torr of OCCl₂ is irradiated. The upper curve gives the sum of the 3063- and 2580-Å emission efficiencies and the lower curve represents the 3063-Å emission efficiencies.

The threshold for the 2580-Å continuum lies at a nominal incident wavelength at 1497 Å. Since the curve shows no distinct increase near threshold, a rather large uncertainty amounting to ± 10 Å may be involved in the determination, corresponding to 8.28 ± 0.05 eV for the threshold photon energy. The threshold of the incident photons to yield the 3063 Å continuum corre-



FIG. 4. Cl₂ fluorescence efficiencies from photolysis of 0.11 torr of OCCl₂ as a function of incident wavelength: scanning speed, 10 Å per minute; time constant, 5 sec. Upper curve: fluorescence efficiencies for the 2580- and 3063-Å continua; resolution, 3 Å. Vibrational features correspond to the ν_1 progression of OCCl₂ observed in absorption (Ref. 9). Lower curve: fluorescence efficiencies for the 3063-Å continuum; resolution, 8 Å

sponds to a nominal wavelength 1380 Å. Considering the 8-Å bandwidth of the incident photon beam, the actual wavelength may be taken as 1378 ± 4 Å, corresponding to 9.00 ± 0.03 eV. The fluorescence efficiency of the 2580-Å continuum becomes appreciable only below 1380 Å of incident wavelength corresponding to absorption region III. Below about 1340 Å, the curve shows diffuse features corresponding to the ν_1 vibrational progression in Region IV. Below 1250 Å there are several diffuse bands, some of which appear very broad in absorption. Approximate positions of these bands are listed in Table I.

DISCUSSION

It has been shown that a major primary process in the photolysis of OCCl₂ in the vacuum ultraviolet is the detachment of electronically excited Cl₂. A similar molecular detachment process has been found in the vacuum-ultraviolet photolysis of H₂O, producing an electronically excited H₂,¹⁰ and of H₂CO,¹¹ CH₄,¹² NH₃,¹³ H₂O,¹³ and C₂H₆ ¹⁴ yielding the ground-state H₂. Figure 4 shows that the fluorescence efficiency of the 2580-Å continuum is very small near threshold, while the absorption is relatively large [$k\approx1000$ (atm cm⁻¹)] indicating that excited OCCl₂ dissociates mainly to produce products other than electronically excited Cl₂.

The fluorescence efficiency curve starts to increase below 1400 Å, corresponding to Region III in absorption. No vibrational structure is apparent in the curve corresponding to the ν_3 progression in absorption. However, the vibrational features, corresponding to the ν_1 mode in Region IV, can be seen in the fluorescence

efficiency curve. This indicates that the main electronic transition to produce Cl₂* takes place in Region IV and that at least two transitions are involved in Region III, one of which is correlated with the ν_3 progression, but does not produce Cl₂*. The fluorescence efficiency is strongest in Region V (1190–1270 Å) which is also the region of highest absorption. Several peaks listed in Table I are apparent in absorption in this region. The first five peaks starting at 1250 Å towards shorter wavelength appear to form the ν_1 progression with the mean frequency of about 760 cm⁻¹ within a large experimental error of ± 100 cm⁻¹. Since not all vibrational features present in absorption appear in the fluorescence efficiency curve, absorption of photons in this region must produce at least two electronic states, only one of which dissociates to form Cl_2^* . Vibrational features observed in the fluorescence efficiency curve suggest that the excited state responsible for the production of Cl₂* must have a life of the order of 10^{-12} sec or longer before it dissociates.

Electronic Energies of the Upper States of Cl₂

Three main emission continua of 3063, 2565, and 2432 Å have been observed by Elliot and Cameron⁴ in a high-frequency electric discharge of Cl₂, but no spectroscopic analysis was given of the transitions involved. Venkateswarlu¹⁵ interpreted these emissions as arising in transitions from bound upper states to lower repulsive states producing two ²P chlorine atoms. Electronic energies of the upper states were estimated to be 58 000 cm⁻¹ (7.19 eV) and 67 700 cm⁻¹ (8.39 eV) for the 3063- and 2565-Å continuum, respectively.

While essentially the same emission continua were excited by active nitrogen,⁵ relative intensities of the maxima were different. Furthermore, two diffuse vibrational progressions appeared on the 2580-Å continuum. The latter has been ascribed to the transition from a bound upper state to a lower state having a shallow potential minimum. The electronic energy of the upper state giving the 3063-Å continuum was estimated to be about 10 eV. Venkateswarlu and Khanna¹⁶ discovered that the presence of a large amount of Ar in an electric discharge of Cl₂ produced a strong band system in the region 2600-2390 Å and a weak system in the region 2365-2239 Å. From the vibrational analysis of the main system in the region 2600-2390 Å, they concluded that the transition is from the upper state at 57 773 cm⁻¹ (7.163 eV) to the lower ${}^{3}\pi(O_{u}^{+})$ state at 17 658 cm⁻¹ (2.189 eV). From their work it is not clear whether this upper state is identical with any of the states giving emission continua in the absence of Ar. In the flash photolysis of Cl₂ mixed with a large amount of inert gas, Briggs and Norrish¹⁷ found a new transient absorption in the region 2100-2500 Å. From the rotational and vibrational analysis of this system, they reached a conclusion that the transition was from the ${}^{3}\pi(O_{u}^{+})$ to an upper state, probably O_{g}^{+} , located at 57 550 cm⁻¹ (7.135 eV), apparently corresponding to the transition observed by Venkateswarlu and Khanna in emission. Present work shows that the photolysis of OCCl₂ by the Kr 1236-Å line yields three emission continua at 3063, 2565, and 2460 Å, while only one continuum was found at 2580 Å by the Xe 1470-Å line. For the production of two other continua at 3063 and 2460 A, incident photon energies above 8.4 eV, but below 10 eV, are required. The addition of inert gases, N2 and Ar, to OCCl2 produces the same effect as lowering the energy of excitation, resulting in the production of only one narrow continuum at 2580 Å on which diffuse bands are super-

TABLE I. Vibrational structure observed in the fluorescence efficiency curve of $OCCl_2$ in Region V.

Wavelength (Å)	ν (cm ⁻¹)	$\Delta \nu$ (cm ⁻¹)	
 1250	80 000		
		841	
1237	80 841		
		659	
1227	81 500		
		805	
1215	82 305	254	
1204	92 056	751	
1204	83 030	1100	
1187	84 246	1170	
.107	01 210	933	
1174	85 179	200	



FIG. 5. Energy-level diagram of Cl_2 ; transitions producing the 2580- and 3063-Å emissions are indicated. Vibrational levels of the upper and lower states for the 2570-Å emission were drawn after Briggs and Norrish (Ref. 17) and for the 3063-Å emission after Venkateswarlu (Ref. 15) and this work.

imposed. An increase of the peak intensity at 2580 Å and a decrease of the width of the continuum upon addition of the inert gas indicate that higher vibrational levels are deactivated to or near the ground levels of the upper state. Suppose the internuclear distances of the upper and lower states are not much different and the lower state has a shallow minimum as is suggested by Cameron and Elliott,⁵ then the transitions from higher vibrational levels of the upper state would contribute mainly to the continuum and emission originating near ground levels would be expected to produce the diffuse bands. The threshold energy of incident photons to produce 2580 Å has been determined to be 8.28 ± 0.05 eV. The heat of reaction for (3) at 0°K,

$$OCCl_2 \rightarrow CO + Cl_2,$$
 (3)

can be calculated to be 24.69 kcal mole⁻¹ or 1.071 eV.¹⁸ Therefore, the electronic energy of the upper state associated with the 2580-Å continuum is calculated to be 7.21 ± 0.05 eV with respect to that of the groundstate Cl₂. This value, within the specified error limit, is in reasonable agreement with the electronic energy of 7.163 eV obtained by Venkateswarlu and Khanna¹⁶ in emission, and with 7.135 eV calculated by Briggs and Norrish¹⁷ in absorption. From the observed threshold of 1378 ± 4 Å or 9.00 ± 0.03 eV for the production of the 3063-Å emission, the electronic energy of $7.93 \pm$ 0.03 eV is obtained, which is 0.7 eV above the upper state giving the 2580-Å emission. Since no diffuse bands were observed in the 3063-Å continuum,^{4,15} lower states must be repulsive producing two 2P chlorine atoms. An energy-level diagram for the upper and lower states and transitions involved for the production of the 2580- and 3063-Å continua is given in Fig. 5. Vibrational levels of the upper and lower states involved in the production of the 2580-Å emission are drawn according to Briggs and Norrish.17 Since vibrational levels of the upper state giving the 3063-Å continuum overlap with those of the upper state responsible for the 2580-Å continuum, it is likely that the observed effect of inert gas is a collision-induced transition from the former to the latter state. The electronic state giving the 2460-Å emission could not be determined with certainty. Since the emission appeared by the 1236-Å excitation (10.0 eV), but not by the 1470-Å (8.4-eV) excitation of OCCl₂, the state must lie between 7.33 and 8.93 eV. This state is quenched by collisions with the inert gas. Apparently there is no observed absorption band¹⁹ corresponding to transitions to this state¹⁷ from the ground state of Cl₂, indicating that the transition is forbidden by the selection rules. In support of this observation, no emission in the region 1700-6000 Å was detected from Cl_2 excited by photon energies from 6 to 8 eV. Electronic states of Cl2* can also be estimated from reactions with Cl₂ of metastable atoms and molecules of known electronic energy. In a system where those metastable species were produced in a flow electric discharge, it has been shown that the reaction of Ar ${}^{3}P_{0,2}+Cl_{2}$ produced strong emission at 2580 Å,²⁰ while no emission was observed from reactions N_2 A $^3\Sigma\!+\!\operatorname{Cl}_2$ and CO $a \,{}^{3}\pi + \operatorname{Cl}_{2}$, although N₂ $A \,{}^{3}\Sigma$ and CO $a \,{}^{3}\pi$ were rapidly quenched.6 This is contrary to the observation by Provencher and McKenney²¹ that the Cl₂ 2580-Å continuum was found in the reaction N₂ A ³ Σ +Cl₂. Since the electronic energy of the upper state associated with the 2580-Å emission is 7.21 ± 0.05 eV and those of N₂ A ³ Σ and CO a ³ π are 6.22 and 6.04 eV, respectively,²² it is obvious that the emission cannot be excited by the reactions, N₂ $A^{3}\Sigma + Cl_{2}$ and CO $a^{3}\pi + Cl_{2}$. Excited species other than $N_2 A \ ^3\Sigma$ must be responsible for the production of the Cl_2 2580-Å emission in the latter work.

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