Quenching Rates for Metastable Oxygen Atoms ($^5S^0$)

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(Z. Naturforsch. **28 a**, 725—729 [1973] ; received 4 January 1973)

Metastable O (3s $^5S^0$) atoms were produced by rare gas sensitized decomposition of various oxygen containing compounds. The quenching rate constants of H_2, N_2, O_2, NO, N_2O, N_2O_4/NO_2, CO, CO_2, SO_2, SO_3, H_2O and the noble gases for the 0 (^5S) have been measured by absorption spectroscopy. The noble gases, except xenon, deactivate the metastable oxygen atom with low collision efficiency. Xenon and molecular gases, except hydrogen, deactivate this species efficiently, the cross section being of the order of gas kinetic cross sections.

Introduction

It is of great interest to obtain information about deactivation processes by which the inner energy of atoms or molecules is transferred to a surrounding medium. Knowledge of these reactions, apart from being of certain theoretical interest, is of importance for practical purposes in radiation and plasma chemistry.

This work was undertaken to measure deactivation efficiencies for oxygen atoms in the $2p^3$ 3s $^5S^0$ state by several simple gases. These data may be compared with the rate constants for the deactivation of O ($2p^4$ ^1D) [1] and O ($2p^4$ ^1S) [2]. Some of these data may also be of importance for the interpretation of reactions in the upper atmosphere where these oxygen atoms are present as indicated by the multiplet emission at 135.6 nm in the aurora and in the dayglow.

Recently the production of O(^5S) by electron impact on CO [3], CO_2 [4–6], O_2 [7, 8] and H_2O [9] was described and some emission cross sections were measured. In the present investigation, the O(^5S) was produced by rare gas sensitized decomposition of various oxygen containing compounds. The deactivation rate constants were obtained by kinetic spectroscopy.

Experimental

The pulse radiolysis method used is described in detail elsewhere [10].

The gas mixtures were prepared by vacuum line operations and irradiated in a stainless steel cell (4.5 l) with electron pulses from a Febetron 706 machine (600 keV, 3 nsec halfwidth, 10 Joule). All experiments were carried out at room temperature.

For identification purposes the absorption spectra of intermediates were taken immediately after the excitation by flash photography on Kodak IR film. The halfwidth of the lightflash was about 2 μsec.

The continuous analyzing light passed the cell via an internal White system. The reflecting surfaces of the mirrors were gold coated. The light was reflected into a 75 cm spectrograph from Spex (1800/II). A grating blazed at 500 nm with 1200 grooves/mm was used. The average spectral resolution was 0.1 nm which was quite sufficient in most cases because the atomic lines were broadened in the presence of 1 – 3 atm of helium. For the photographic measurements the length of the lightpath through the reaction zone was 8 m.

The time dependence of the absorbance or emission intensity was followed by an electronic detection system which was normally operated with a time resolution of about 20 nsec using a C 31025 C (RCA) photomultiplier (200 Ω load resistance). The lightpath was 2 m. The electric signal was displayed on a 250 MHz oscilloscope (HP 183).

Single events were measured and the polaroid photographs of the oscilloscope screen evaluated by hand after enlargement.

High purity rare gases, helium N 56, neon N 45 and argon N 48 were further purified by passage through an Oxisorb trap (Messer Griesheim) and then through a low temperature (77 K for He, Ne and 193 K for Ar) column filled with activated molecular sieve and active carbon. Krypton N 47 and xenon N 47 were distilled at the vacuum line.

The additives CO_2, SO_2, SO_3, N_2O, NO, NO_2 and H_2O were purified by bulb to bulb distillation while O_2, N_2 and CO were evaporated from the liquid.

The O(^5S) was followed spectroscopically by the multiplet absorption (3p ^5P – 3s $^5S^0$) at 777.2 nm.

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The measurement of the deactivation of a species which is produced by sensitized excitation appears to involve certain difficulties. The rate constant for deactivation might be found smaller than the true value because of long lasting production channels. In order to exclude interference through a population of the $O(^5S)$ state by $O(^5P)$, experimental conditions were chosen such that the decay rate of the $O(^5P)$ emission was faster than the disappearance of the $O(^5S)$.

Results

When 1 – 3 Torr of pure oxygen was irradiated by an electron pulse, neither the absorption of $O(^5S)$ nor any other absorption of oxygen was observed photographically or photoelectrically. Yet if a noble gas was added to an oxygen containing compound the absorptions and emissions of O I could be seen. The transitions observed photographically are given in Table 1. Besides these absorptions of oxygen atoms, absorptions of metastable atoms and molecules of the noble gases appeared.

Figure 1 shows as an example the kinetic behaviour of all species cited in Table 1 and of He_2 $(a\,^3\Sigma_u^+)$, the longest lived excited species of helium in a He/O_2 mixture[11]. The optical densities taken from the enlarged oscillograms were plotted after first order. In all experiments involving the disappearance of $O(^5S)$ the linearity of the first order plot indicated that processes of higher order were not involved. The inverse time constants $1/\tau$ taken from those plots depended linearly on the additive pressure. This was interpreted as pseudo first order deactivation of the $O(^5S)$ by the additive. $1/\tau$ was then plotted against the pressure of the reactant and the rate constants for the quenching of the $O(^5S)$ were derived fom such Stern-Volmer plots.

Figure 1 shows that the time constant for disappearance of the $O(^5S)$ in this He/O_2 mixture is similar to that of $O(^3D)$, $O(^5P)$ and $He_2(a)$. The decay of the $O(^5S)$ is very likely perturbed by a formation mechanism.

Inspite of the purification the absorption of $O(^5S)$ was still observed upon irradiation of helium, neon and argon. Probably this was caused by residual impurities. Argon contained small traces of krypton and xenon as indicated by the absorptions of the metastables Kr $(5s[1\ 1/2]^\circ)$ and $(5s'[1/2]^\circ)$ and Xe $(6s[\ 1\ 1/2]^\circ)$ and krypton showed traces of xenon.

The absorption produced from impurities was of sufficient intensity so that rate constants for the deactivation of $O(^5S)$ by helium, neon and argon could be measured without adding oxygen containing compounds.

If a substance did not produce $O(^5S)$ and showed an efficient deactivation of it, for example Xe, N_2 and Kr, usually a three component mixture was used. For hydrogen an addition of nitric oxide appeared to give side effects by rapidly producing an efficient scavenger for $O(^5S)$ upon irradiation. Therefore experiments were made only with helium /hydrogen mixtures where the $O(^5S)$ was produced from impurities.

In 2200 Torr of purified helium the lifetime τ of the $O(^5S)$ was found to be 109 μsec. The lifetime of He_2 $(a, v=0)$ was about 25 μsec. In this case no interference by this metastable species occurs. Variation of the helium pressure from 760 to 2200 Torr did not show an influence on the rate of deactivation within experimental error. Contrary to the helium observations in 2200 Torr of neon and argon the lifetimes of $O(^5S)$ were shorter (16.5 μsec and 2.2 μsec respectively), yet the variation of the rare

Table 1. Photographically observed absorptions * and emission of O I in mixtures of oxygen and water (about 0.5 torr) with noble gases (about 760 torr) immediately after excitation by a 600 keV electron pulse. The lightpath was 8 m.

	Absorption of				Emission of
	$3s'\,^1D^0$	$3s'\,^3D^0$	$3p\,^5P$	$3s\,^5S^0$	$3p\,^3P$
Transition	$3p\,^1D$ — $3s'\,^1D^0$	$3p'\,^3F$ — $3s'\,^3D^0$	$4d\,^5D^0$ — $3p\,^5P$	$3p\,^5P$ — $3s\,^5S^0$	$3p\,^3P$ — $3s\,^3S^0$
(eV)	(14.46) (12.73)	(14.10) (12.54)	(12.75) (10.74)	(10.74) (9.12)	(10.99) (9.52)
Wavelength [nm]	715.68	795.0 (multiplet)	615.7 (multiplet)	777.4 (multiplet)	844.6 (multiplet)
He/O_2	×	×	×	×	×
Ne/O_2	—	—	×	×	×
Ar/O_2	—	—	—	×	—
Kr/O_2	—	—	—	×	—
He/H_2O	—	×	—	×	×

* The limit of detection was $\ln I_0/I=0.01$.

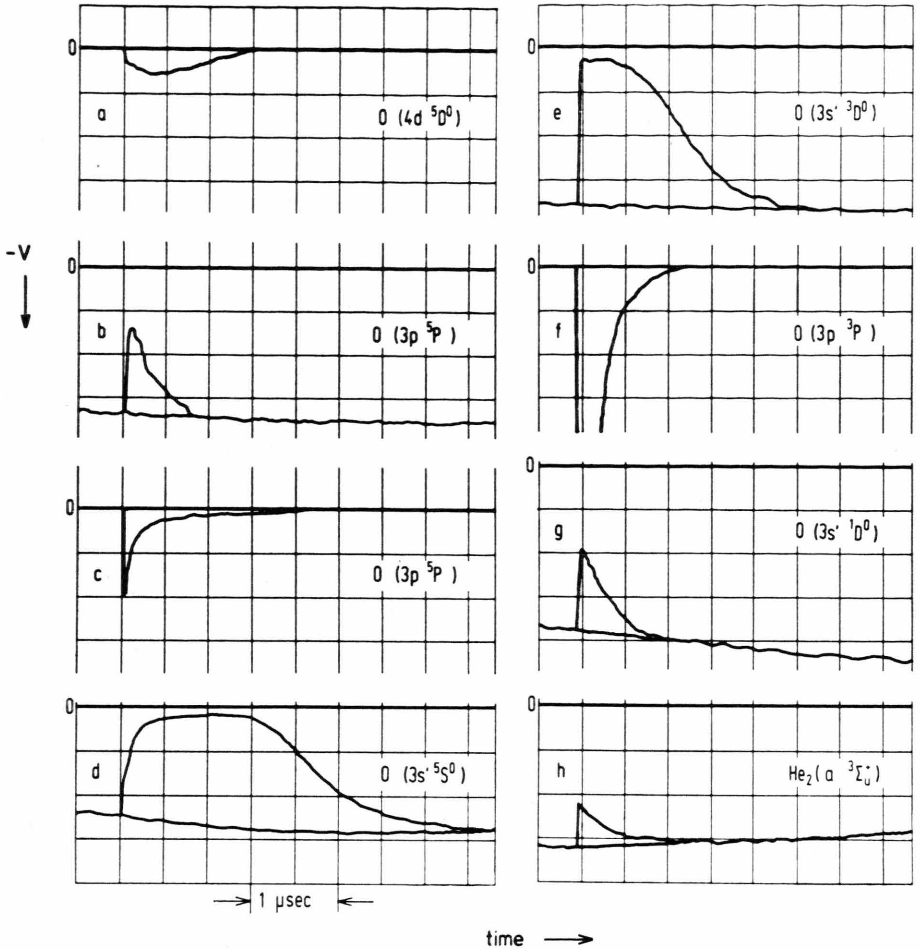

Fig. 1. Oscilloscope traces of absorptions (b, d, e, g, h) and emissions (a, c, f) of intermediates formed in a mixture of 0.48 torr O_2 and 1500 torr He irradiated with an electron pulse. The wavelengths for the oxygen species are given in Table 1, the He_2 ($a\ ^3\Sigma_u^+$, $v=0$) was measured at 805.37 nm. The absorbed energy was 7.5×10^{18} eV/pulse.

gas pressure gave lower limits for the rate constants than expected from the lifetimes. Probably long lived metastable rare gas species were the main deactivating source. Rate constants and upper limits of rate constants for the deactivation of O(^5S) by noble gases are given in Table 2.

Table 3 shows the rate constants for quenching of the O(^5S) by molecules. For hydrogen the rate constant for the disappearance depended on the number of pulses given to a filling and increased by more than a factor of two after the first pulse. Therefore, only an upper limit can be given for the rate constant.

In order to evade the perturbation in helium/oxygen mixtures (Fig. 1) the rate constant for deactivation of the O(^5S) by oxygen was measured in a three component system. In mixtures of helium/car-

Table 2. Rate constants for the quenching of O ($^5S^0$) by noble gases measured in irradiated additive/noble gas mixtures. Collision efficiencies were calculated with the atomic diameters and formula given in Landolt-Börnstein [12].

noble gas	torr	additive	torr	k cm^3/sec	collision efficiency
He	2200	—	—	$<5.4\times10^{-17}$	2.2×10^{-7}
Ne	760–2200	—	—	$<2.8\times10^{-16}$	1.6×10^{-6}
Ar	760–2200	—	—	$<5.8\times10^{-15}$	2.6×10^{-5}
Kr [a]	150–300	H_2O	<0.07	2.2×10^{-13}	1.2×10^{-3}
Xe [a]	3–5	NO	0.45	9.0×10^{-11}	0.4

[a] Experiments were carried out in the presence of 1500 torr helium.

bon monoxide the decay of the O(^{5}S) was much slower than that of the other species and the addition of small amounts of oxygen did not alter this condition.

Table 3. Rate constants for the quenching of O($^5S^0$) by several gases in the presence of helium. Collision efficiencies were calculated with the molecular diameters and formula given in Landolt-Börnstein [12].

	gas torr	helium pressure torr	$k \times 10^{10}$ cm^3/sec	collision efficiency
H_2	0.15−0,3	1500	0.13	0.07
N_2 [a]	1 −2	1500	0.24	0.09
CO	1 −4	770	0.48	0.17
NO	0.48−4.5	1500	1.1	0.45
O_2 [b]	0.35−0.9	1500	1.4	0.5
N_2O	0.6 −4.2	1500	2.5	0.8
CO_2	0.7 −1.9	1500	4.8	1.6
N_2O_4/NO_2	0.2 −3.6	1500	4.8	—
SO_3	0.5 −3.8	1500	5.2	1.1
SO_2	0.4 −1.8	1500	6.5	2.1
H_2O	0.4 −2.9	1500	7.0	1.8

[a] Measurements were made in the presence of 0.5 torr NO.
[b] Measurements were made in the presence of 0.48 torr CO.

Discussion

Appearance of O(^{5}S)

It is quite surprising that the O(^{5}S) was not found after the pulsed excitation of pure oxygen since it is known from other studies [7, 8] that this species is formed upon electron irradiation. Probably the yield obtained in the present experiments was too low.

The observation of the absorptions from O(^{5}P, ^{3}D and ^{1}D) in the helium sensitized excitation of oxygen has to be explained by some reproduction mechanism because the radiative lifetimes are much shorter than the measured lifetimes ($\tau\,[O(^3D)] = 1.9$ nsec [13]). Such phenomena are well known in rare gas plasmas and can be the result of several processes like resonant radiation imprisonment, reexcitation of a long lived lower state by hot electrons, population from higher excited neutrals and ion-electron recombination. They may also be produced directly from oxygen-containing compounds by energy transfer from rare gas metastables. In Fig. 1 this complication is demonstrated by the kinetic behaviour of several intermediates during the first microsecond after the excitation of a helium/oxygen mixture.

The rare gas used for sensitization plays a significant role in producing the excited oxygen species (see Table 1).

The O(^{5}S) for example was produced from water in mixtures with helium, neon and argon but not with the other rare gases.

Disappearance of O(^{5}S)

The radiative lifetime of the O(^{5}S) was predicted theoretically by Garstang [13] to be around 600 μsec and was measured by Johnson [14] as 185 μsec. Its inner energy of 9.12 eV is sufficient to induce electronic excitation in all substances except helium, neon, argon and krypton.

Deactivation in these rare gases occurs either by collision induced radiative transition to a lower electronic level of oxygen or deexcitation by an electronic-translation (E-T) energy transfer. These processes must have low probabilities compared with electronic-electronic (E-E) energy transfer (Table 2), but no theoretical approach has been found so far. Three possibilities exist for the final state of the oxygen atom, the two metastable singlet states (2p^4 ^{1}S and 2p^4 ^{1}D) and the groundstate (2p^4 ^{3}P). Probably the transition to the groundstate is the preferred reaction path so that the total energy of 9.12 eV is distributed between the reaction partners. The quenching cross section sometimes shows a correlation to a physical property of the deactivating gas, for example, the polarizability [15]. So far such a relationship has not been found.

For molecular gases and for xenon an E-E energy transfer is possible. For molecules especially, many energy levels exist and resonance processes will occur. The comparatively large collision efficiencies for the deactivation of O(^{5}S) by xenon and molecular gases (Table 2 and 3) are in accordance with this scheme.

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Microwave Spectrum and Quadrupole Coupling Constants of 2-Chlorothiophene

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(Z. Naturforsch. **28 a**, 729–738 [1973]; received 18 January 1973)

The microwave spectra of the two chlorine isotopic species of 2-chlorothiophene have been measured in the region 26 500–40 000 MHz.

For both isotopic species, the rotational constants of the ground state and one vibrationally excited state were determined, as well as the centrifugal distortion coefficients of the ground state.

From the hyperfine splitting of the rotational lines, the nuclear quadrupole coupling constants were calculated. The values in MHz are for ^{35}Cl:

$$\chi_{aa} = -74.77 \pm 0.05, \quad \chi_{bb} = 37.51 \pm 0.17, \quad \chi_{cc} = 37.25 \pm 0.18,$$

and for ^{37}Cl:

$$\chi_{aa} = -58.98 \pm 0.09, \quad \chi_{bb} = 29.55 \pm 0.26, \quad \chi_{cc} = 29.43 \pm 0.28,$$

in the principal-axes system of the molecule.

Introduction

The subject of substitution-induced ring-structure deformations has attracted the interest of many workers. In an attempt to estimate the magnitude of the effect for thiophene, Harshbarger and Bauer[1] studied 2-chlorothiophene and 2-bromothiophene by electron diffraction in the gas phase. They found that two slightly different structures, A and B, could be equally well reconciled with the experimental data. Both of these structures were distorted and did not show C_{2v} symmetry.

In a critical analysis of Harshbarger's and Bauer's work, Derissen, Kocken and van Welden[2] questioned the validity of these results. On the basis of a recalculation of Harshbarger's and Bauer's data, they claimed to have shown that a structure having C_{2v} symmetry or even a completely undistorted structure would fit the data equally well. The question regarding the amount of ring distortion in thiophene thus remained unsettled.

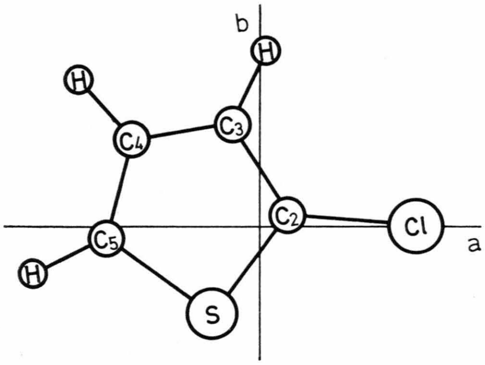

Fig. 1. 2-chlorothiophene.

Table 1 shows the parameters of the different structures proposed by the above-mentioned authors together with the corresponding calculated rotational constants. From these calculations we conclude that none of the structures suggested so far will give correct values for the rotational constants unless very special values are assumed for the experimentally undetermined angles S – C – H and C – C – H. We find no reason to expect a strong deviation of these angles from those of unsubstituted thiophene. Of course, one should not anticipate that the electron diffraction and microwave results agree precisely, because of the well-known differences in the types of averages which are determined. However, the deviations between the calculated and the observed constants are probably too large to be accounted for in this way. Thus, the most reasonable conclusion seems to be that the true ring structure of 2-chlorothiophene is intermediate between the structures proposed by Harshbarger and Bauer and that of thiophene itself.