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GAS PHASE CHEMILUMINESCENT REACTION OF OZONE WITH FURAN

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Summary

The chemiluminescent reaction of ozone with furan was studied in the gas phase at low pressure. Fluorescence was observed from the first excited singlet states of *cis*- and *trans*-glyoxal in addition to phosphorescence from *trans*-glyoxal. The internal rotation energy barrier for *trans–cis* isomerization in the first excited singlet state was estimated to be about 5000 cm^{-1}. The mechanism for the formation of excited species is discussed.

1. Introduction

Furan and its derivatives comprise an industrially significant class of heterocyclic compounds. They are used as selective solvents in a variety of industrial applications. They are released from automobile and diesel exhausts, from the manufacture of fish oil and from forest fires [1]. Recently, furan has been detected in volatile human serum [2], molasses [3], meat [4] and tobacco smoke [5]. Furan has even been detected in ambient air [6]. This has led us to study the chemiluminescent reaction of ozone with furan.

Pitts and coworkers [7] were the first to observe chemiluminescence from the reaction of ozone with 2,5-dimethylfuran but no spectrum was reported. In this work, we present detailed studies on the spectral analysis of the emission in the reaction with furan. Fluorescence from the first singlet states of *cis*- and *trans*-glyoxal has been observed for the first time in the chemiluminescent reactions. The mechanisms for the formation of excited species are discussed.

2. Experimental details

The experimental system has been described in detail earlier [8]. It consists mainly of a quartz reaction cell coupled to a 0.25 m monochromator (Jarrel–Ash). Ozone in oxygen from a Welsbach-type ozone generator was

mixed with the reactant at low pressure, and the light emissions were detected with a photomultiplier tube (EMI 9635 QA). A dual-channel photon counter was used for processing the signal.

Furan vapour was introduced directly from the reactant reservoir. The pressure in the reaction cell was measured with an MKS Baratron pressure sensor (type 310 BHS-1000). Furan (Reidler, Hanover) was distilled before use.

3. Results

Figure 1 shows the chemiluminescence spectrum from the reaction of ozone with furan. The emission starts at about 370 nm and extends up to 600 nm. The peaks in the emission spectrum at 455 nm and 477.6 nm are attributed respectively to the 0_0^0 and 8_1^0 bands of the $^1A_u \rightarrow {}^1A_g$ transition of trans-glyoxal. The peak at 487.5 nm is due to the 0_0^0 band of the $^1B_1 \rightarrow {}^1A_1$ transition of cis-glyoxal. The other three bands at 520 nm, 551 nm and 573 nm are respectively the well-known 0_0^0, 4_1^0 and 2_1^0 transitions of the $^3A_u \rightarrow {}^1A_g$ band system of trans-glyoxal.

The spectra were also recorded at total system pressures of 6, 10, 30 and 62 Torr. This was done by throttling the pumping speed so that the relative concentration of oxygen, ozone and furan remained constant, i.e.
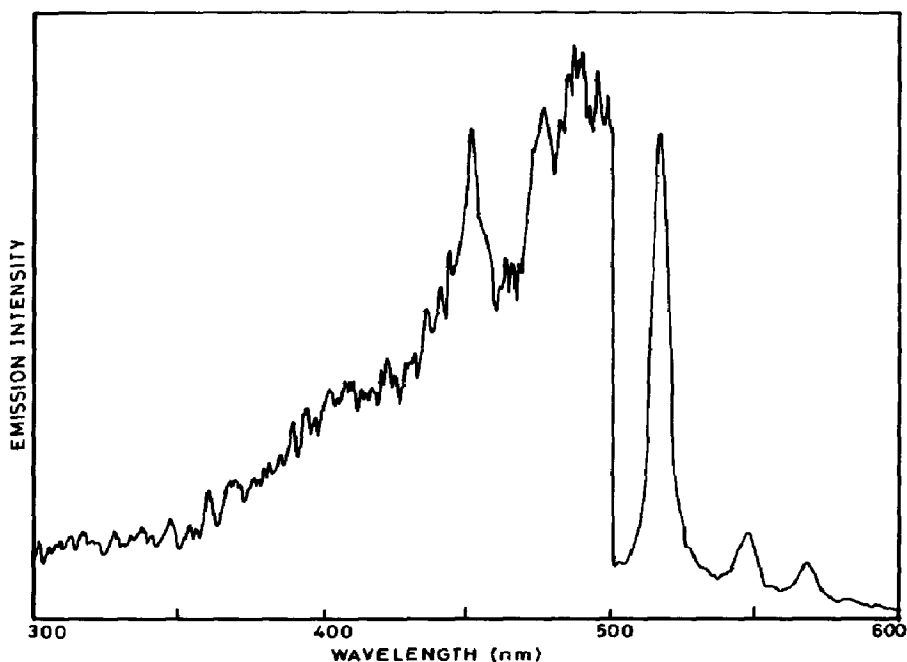

Fig. 1. Chemiluminescence spectrum from the reaction of ozone with furan (spectral slit width, 3.3 nm; 200 counts s^{-1} (300 - 500 nm); 2000 counts s^{-1} (500 - 600 nm); total flow, 105 cm^3 min^{-1}; ozone pressure, 0.11 Torr; furan pressure, 1.43 Torr; total pressure, 7.5 Torr).
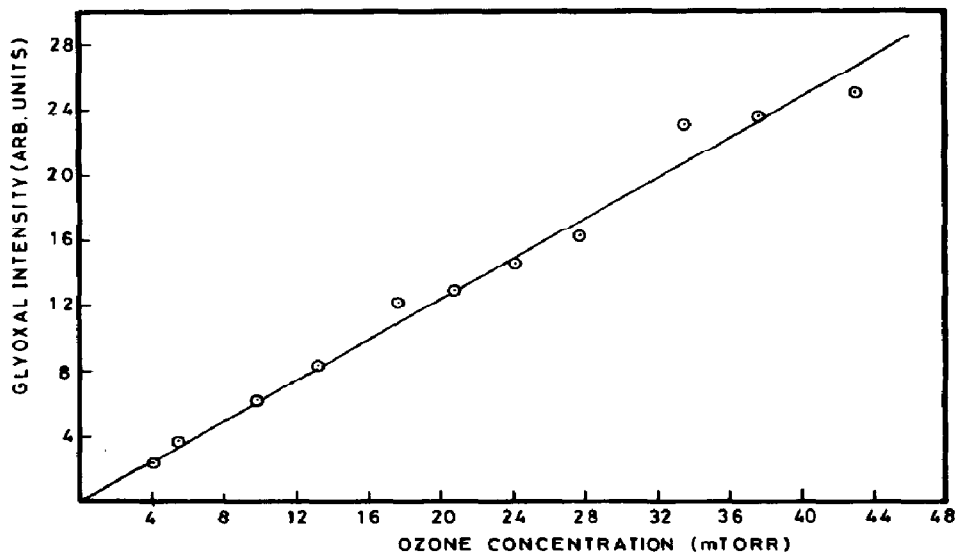
Fig. 2. Effect of the ozone concentration on the glyoxal emission (furan pressure, 1 Torr; total pressure, 3.6 Torr).

50:1:10 respectively. The intensity ratios of the 0_0^0 bands of the triplet transition at 520 nm and the singlet transition at 455 nm were determined from the spectra and were found to be 22, 21.6, 14.5 and 12.4 at total pressures of 6 Torr, 10 Torr, 30 Torr and 62 Torr respectively.

In order to understand the kinetics of the reaction we studied the dependence of the chemiluminescence intensity on the ozone pressure with the pressures of oxygen and furan kept constant. This plot is shown in Fig. 2. The signal is observed to increase linearly with the ozone pressure, demonstrating that the formation of the excited species is first order in ozone.

4. Discussion

In the reaction of ozone with furan we have observed bands of nearly equal intensity at 455 and 477.6 nm. These are due to the 0_0^0 and 8_1^0 transitions of the $\tilde{A}\,^1A_u \to X\,^1A_g$ ($n \to \pi^*$) system of trans-glyoxal [9]. The 0_0^0 ($v_{00} = 22\,000$ cm^{-1}) transition is relatively weak with an oscillator strength f of about 4×10^{-5} even though it is symmetry allowed [10]. For glyoxal with C_{2h} symmetry, $B_u \to A_g$ transitions are also symmetry allowed. Strong vibronic interactions are therefore observed in glyoxal for the C—H wagging mode v_8 since this mode has b_g symmetry and $A_u{}^e \times b_g{}^v = B_u{}^{ev}$. As a result the 8_1^0 band in emission and the 8_0^1 band in absorption are very strong transitions. The ratio of intensities of the 0_0^0 and 8_1^0 bands in emission has been determined [11] to be 1:0.85, which agrees with the present observation.

In the present study we have observed glyoxal emission starting at 370 nm (see Fig. 1). This corresponds to an excess vibrational energy of 5050 cm^{-1} above the 0_0^0 band of the ^1A_u state of glyoxal. The lifetime of the

individual vibronic levels was first studied by Beyer *et al.* [12] and they found that it decreases from 2.41 μs for the 0_0^0 transition to 0.82 μs for the $2_0^1 8_0^1$ transition (excess vibrational energy, 2126 cm^{-1}). Van der Werf *et al.* [13] studied the fluorescence decay behaviour of glyoxal at various excitation energies. At high excitation energies (2417 $cm^{-1} < E < 4343$ cm^{-1}) they observed a fast fluorescence component (lifetime, between 11 and 4.5 ns) in addition to the slow component. They explained this as being due to the strong vibronic singlet–triplet mixing which occurs only at higher excitations as a result of an increasing triplet level density. Recently, Nakamura *et al.* [14] have reported similar results when they observed multicomponent decays while they were studying the effect of an external magnetic field on the time-resolved fluorescence spectra of the single vibronic levels of glyoxal. They were also able to observe the direct emission from the excited level to the ground state just after the excitation. In the present work, the excess vibrational energy of 5050 cm^{-1} in the singlet manifold may therefore reduce the fluorescence lifetime of the states to less than 4.5 ns. Compared with this the time between hard-sphere collisions of glyoxal (molecular diameter, 4 Å) with oxygen (molecular diameter, 3.5 Å) is about 16 ns at a system pressure of 7.5 Torr. Therefore a good fraction of the excited molecules will fluoresce before a collision takes place. This may be responsible for the greater intensity of the broad integrated emission observed compared with those of the bands at 455 and 477.6 nm. It was also observed that the intensity of these bands relative to the integrated emission increased when the system pressure was increased. This is due to the increase in the number of collisions at higher system pressures, which results in the de-excitation of the higher vibronic levels to the zero-point level of the ^1A_u state.

The peak at 487.5 nm has been assigned to the $^1B_1 \rightarrow {}^1A_1$ transition of *cis*-glyoxal. In the ground electronic state the energy difference between the *cis* and the *trans* isomers has been estimated by Currie and Ramsay [15] as $E_{cis} - E_{trans} = 1125 \pm 100$ cm^{-1}. However, the 0_0^0 band of the first singlet–singlet transition in the *cis* isomer is displaced towards the red by 1460 cm^{-1} with respect to that of the *trans* isomer. The $^1B_1$ state of *cis*-glyoxal thus lies about 335 cm^{-1} below the ^1A_u state of the *trans* form, and *trans*–*cis* isomerization cannot be excluded. The energy E' of the internal rotation barrier for isomerization in the ground state has been estimated theoretically to vary between 1800 and 2700 cm^{-1} [16 - 20]. Cossart-Magos *et al.* [11] have estimated the energy E'' of the barrier for the isomerization process in the excited state on the assumption that the excited molecule is in thermal equilibrium with the environment. By assuming that the frequency v_7' of the torsional vibration is equal to the pre-exponential factor they obtained $E'' \approx 4000$ cm^{-1} as a lower limit of the potential energy barrier. Such an increase in the barrier height in the excited state could be expected from considerations of the electronic structure of the n,π^* state and is directly suggested by the higher value of the torsional frequency in the ^1A_u state ($v_7' = 233$ cm^{-1}) compared with that of the ^1A_g state ($v_7'' = 127$ cm^{-1}). A rough estimation of E'' based on this frequency change gives $E'' \approx 3700$ cm^{-1}

[21]. Since in the present study the excess vibrational energy in the singlet manifold is of the order of 5000 cm^{-1}, *trans–cis* isomerization can take place and it may be responsible for the observation of fluorescence from *cis*-glyoxal. The potential energy barrier for isomerization in the excited state can therefore be estimated to be about 5000 cm^{-1}. A further study of the photophysical properties of *cis*-glyoxal will be useful to determine the value of E''.

The peaks at 520, 551 and 573 nm are due to phosphorescence from the ^3A_u state of *trans*-glyoxal. The ^3A_u state of glyoxal is supposed to be formed from ^1A_u by collision-induced intersystem crossing. Anderson *et al.* [22] have studied the effect of increasing pressures of foreign gases on the glyoxal ^1A_u and ^3A_u emissions, and they observed that singlet emission was selectively quenched while triplet emission was slightly enhanced. This was interpreted as due to the collision-induced intersystem crossing $^1A_u \rightsquigarrow\!\!\rightarrow {}^3A_u$. Recently, Michel and Tramer [23] observed that intersystem crossing is absent in collision-free conditions for glyoxal-d_2 and glyoxal-h_2. These conclusions are consistent with the predictions of the theory of non-radiative transitions in the resonant limit for small molecules [24].

We propose the following reaction mechanism for the formation of excited glyoxal:

$$(1)$$

$$(2)$$

$$G(^1A_u) + O_2 \xrightarrow{k_4} G(^3A_u) + O_2 \tag{3}$$

$$G(^3A_u) + O_2 \xrightarrow{k_5} G(^1A_g) + O_2 \tag{4}$$
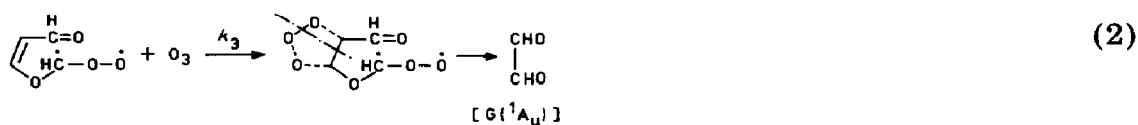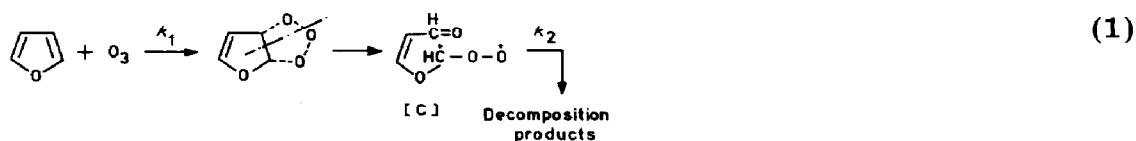
The other loss processes are fluorescence decay (k_f) for the ^1A_u state and phosphorescence decay (k_p) for the ^3A_u state.

Now if we assume that excited glyoxal is formed in the ^1A_u state and steady state concentrations are established for the Criegee intermediate C and for the ^1A_u and ^3A_u states of glyoxal, then

$$[C] = \frac{k_1[F][O_3]}{k_2 + k_3[O_3]} \tag{5}$$

and

$$[G({}^1A_u)] = \frac{k_3[C][O_3]}{k_1 + k_4[O_2]} \qquad (6)$$

Substituting the value of [C] in eqn. (6) and assuming that $k_2 < k_3[O_3]$ we obtain

$$[G({}^1A_u)] = \frac{k_1[F][O_3]}{k_1 + k_4[O_2]} \qquad (7)$$

i.e. the formation of excited glyoxal is first order in ozone.

In the present kinetic treatment, the *trans–cis* isomerization has been neglected because it can be seen from the spectrum that the fluorescence intensity of the *cis* isomer is compatible with only a small concentration of *cis*-glyoxal. Since the furan concentration is small compared with that of oxygen, the quenching of excited states with furan has also been excluded. The steady state concentration of the ${}^3A_u$ state of glyoxal can therefore be written as

$$[G({}^3A_u)] = \frac{k_4[G({}^1A_u)][O_2]}{k_p + k_5[O_2]} \qquad (8)$$

or

$$\frac{[G({}^3A_u)]}{[G({}^1A_u)]} = \frac{k_4[O_2]}{k_p + k_5[O_2]} \qquad (9)$$

The value of k_p ($\approx 3 \times 10^2$ s^{-1} [25]) is much less than $k_5[O_2]$ even for oxygen at a pressure of 1 Torr (since k_5 is 3 ms^{-1} Torr^{-1} for oxygen [25]) and therefore can be neglected. Then

$$\frac{[G({}^3A_u)]}{[G({}^1A_u)]} = \frac{k_4}{k_5} \qquad (10)$$

i.e. the ratio is independent of the oxygen pressure.

The ratio of the emission intensities due to triplet and singlet states of glyoxal would then be

$$\frac{I({}^3A_u)}{I({}^1A_u)} = \frac{k_p k_4}{k_1 k_5} \qquad (11)$$

By substituting the values of k_p, k_1 (2.44×10^5 s^{-1} for the zero-point level of the ${}^1A_u$ state [26]), k_4 (0.86 μs^{-1} Torr^{-1} for oxygen [27]) and k_5 we find that the ratio of the intensities (eqn. (11)) should be 0.35. However, it is observed from the spectrum that the ratio of the emission intensities from the zero-point levels of the triplet state (integrated emission beyond 500 nm) and the singlet state (integrated emission of the 455 and 477.6 nm peaks) is 15. This ratio, when corrected for the spectral response of the system, will be higher still. Even the ratio of the integrated emission from the triplet state (beyond 500 nm) and the singlet state (from 370 to 500 nm) is found to be 2.3. This increase in the concentration of the triplet state is due to the fact that the strong vibronic singlet–triplet mixing occurs at higher vibrational

energies because of the increased triplet level density. Van der Werf *et al.* [13] have calculated the triplet level density at different vibrational energies above the singlet and triplet zero-point levels and have shown that, at higher vibrational energies, the relaxation can be almost classified as statistical limit behaviour. The non-radiative transition between the ^1A_u and ^3A_u states can then take place intramolecularly at a rate which is almost insensitive to collision with other molecules.

As seen from eqn. (11), the ratio of emission intensities should be independent of the oxygen pressure. However, we did find that the ratio of the peak heights of the triplet transition at 520 nm and the singlet transition at 455 nm decreased by a factor of 1.8 when the system pressure was increased tenfold. This is because of an increase in the zero-point population of the ^1A_u state which occurs as a result of the vibrational relaxation of different vibrational levels to the zero-point level on collisions with other molecules [24].

Further studies are under way to measure more accurately the internal rotation barrier for *trans–cis* isomerization in the first excited state of glyoxal using laser excitation.

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