

## PHOSPHORESCENCE OF $\alpha$ -DIKETONES FROM OZONE-OLEFIN REACTIONS

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### Summary

Phosphorescence spectra of  $\alpha$ -diketones in the gas phase have been measured at 3 to 12 Å resolution, and are compared with equally well resolved chemiluminescence spectra from ozone-olefin reactions. Glyoxal phosphorescence could be identified in the chemiluminescence spectra of propene, 1-butene, *cis*- and *trans*-2-butene, and cyclohexene. Methylglyoxal phosphorescence results from the reactions of isobutene, trimethyl-ethylene, and tetramethyl-ethylene. Biacetyl phosphorescence most probably does not contribute to the chemiluminescence of ozone-olefin reactions. The pressure dependence of the phosphorescence from the ozone-tetramethyl-ethylene reaction yields rate constants of  $2.6 \times 10^{-15}$  and  $2.5 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the quenching of methylglyoxal phosphorescence by O<sub>2</sub> and N<sub>2</sub>. The relative pressure dependences of formaldehyde fluorescence, glyoxal phosphorescence and methylglyoxal phosphorescence, as well as their excitation mechanisms are briefly discussed.

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### Introduction

Gas phase reactions of ozone with olefins have been extensively studied in recent years to evaluate their role in atmospheric chemistry [1 - 3]. Direct evidence of excited product and radical formation in these reactions was first obtained from the accompanying chemiluminescence which had been used for the detection of atmospheric ozone in chemiluminescent analyzers even before the emitting species were identified [4]. It has since been established [5, 6] that electronically excited formaldehyde, giving rise to the A <sup>1</sup>A<sub>2</sub> → X <sup>1</sup>A<sub>1</sub> band system above 3500 Å, as well as vibrationally excited OH X <sup>2</sup>Π<sub>i</sub> radicals are products common to all ozone-olefin reactions which have been studied. The latter radicals are produced by secondary reactions of H atoms with ozone and are detected by their emission of the Meinel bands in the red and infra-red part of the spectrum. When alkyl substituted olefins are reacted

with ozone, a third emission is observed which appears as a single band at 5200 Å at low resolution. Only in the case of the 2-butenes has this band been positively identified as glyoxal phosphorescence by a comparison of the band contours with the known phosphorescence spectrum of the pure compound [6]. Other published spectra from reactions of olefins bearing two methyl groups at one carbon atom of the double bond show a somewhat broader band at approximately the same wavelength which has been tentatively assigned to methylglyoxal phosphorescence [6]. The emission could not be obtained under sufficient resolution to make a positive identification. Rather weak phosphorescence spectra of pure methylglyoxal, to which a comparison could be made, have been published only recently by Coveleskie and Yardley [7].

Phosphorescence spectra of the pure  $\alpha$ -diketones in question are presented in this paper and compared with well resolved spectra from ozone-olefin reactions. Some information on the pressure dependence of these emissions is also presented.

## Experimental

Chemiluminescence was produced in a 50 cm long cylindrical reactor of 6 cm diameter by the reaction of various olefins with ozonized oxygen ( $\leq 7\%$  ozone) at pressures ranging from  $<1$  to 200 Torr. The gases were introduced radially through concentric tubes and mixed in front of an end window of the flow tube. The latter was mounted in the optical axis of a Spex 1704 monochromator. The optical detector consisted of a liquid nitrogen cooled EMI photomultiplier (either 9558 B or 9659 QB) in conjunction with a fast pre-amplifier, a discriminator, and a ratemeter.

Pressure dependences were studied in an "inverted chemiluminescent ozone analyzer" consisting of a light tight Teflon reaction chamber of 233 ml volume, viewed by an EMI 9635 QB photomultiplier with a bialkali photocathode. Ozonized oxygen and olefins at concentrations  $\leq 1$  p.p.m. in a carrier gas were mixed close to the front window of the chamber. The total pressure could be varied at constant mass flow rates which were measured with precision flow meters.

Phosphorescence spectra of  $\alpha$ -diketones were excited by energy transfer from triplet  $\text{SO}_2$  to the pure compounds. Electronically excited  $\text{SO}_2$  was generated in the flow tube by the chemical reaction of SO with ozonized oxygen. SO was obtained from a microwave discharge in argon containing a low percentage of  $\text{SO}_2$ . The distance between the discharge and the mixing region in the flow tube was chosen long enough to remove oxygen atoms which are also produced in the discharge by wall reactions. Their presence is easily detected by the blue recombination afterglow with SO. Very strong chemiluminescence from both the singlet and triplet states of  $\text{SO}_2$  was observed when ozonized oxygen was admixed in the flow tube. The gas flow rates and the total pressure were then optimized to yield the maximum  $\text{SO}_2$  phosphorescence intensity by collision induced intersystem crossing. The

vapours of the  $\alpha$ -diketones in argon were subsequently added from thermostated saturators containing the pure compounds. Efficient energy transfer resulted in complete quenching of the  $\text{SO}_2$  chemiluminescence, being replaced by intense phosphorescence emission from the diketones. Spectra were recorded through a 4900 Å cut-off filter at constant phosphorescence intensity. The latter was monitored by a second photomultiplier through a suitable interference filter. A slow but steady loss of intensity during prolonged operation of the system was caused by the deposition of a brown polymer on the quartz window closest to the mixing zone.

### Chemicals

Glyoxal was prepared by depolymerization *in vacuo* of the trimeric compound in the presence of phosphorus pentoxide. Methyl glyoxal (pyruvaldehyde) was obtained by  $\text{SeO}_2$  oxidation of acetone, following the procedure of Steinbauer and Prey [8]. Both  $\alpha$ -diketones were purified by fractional bulb to bulb distillation on the vacuum line in the presence of phosphorus pentoxide, and stored at  $-78^\circ\text{C}$ . Biacetyl (Aldrich Chemicals, 99% pure) was used as received.

## Results and discussion

### *trans*-Glyoxal phosphorescence

A phosphorescence spectrum of glyoxal, obtained at 3.2 Torr total pressure by the energy transfer method with triplet  $\text{SO}_2$ , is presented in Fig. 1(b). The spectral slit width was 3 Å. Our assignment of prominent vibronic bands follows previous work by Ramsay *et al.* [9] who investigated the magnetic rotation spectrum as well as laser induced emission spectra of glyoxal. For comparison, a chemiluminescence spectrum from the reaction of 6.8 Torr propene with 2 Torr ozonized oxygen is also shown in Fig. 1(a). The spectral slit width was 8 Å. There can be no doubt, in spite of the somewhat poorer signal to noise ratio in Fig. 1(a), that both spectra belong to the same emitter. Equally well resolved glyoxal bands were recorded in the chemiluminescence spectra of ozone with *cis*- and *trans*-2-butene, 1-butene and cyclohexene. The chemiluminescence spectrum of the 1,3-butadiene-ozone reaction also showed a weak narrow band at  $\sim 5200$  Å which could not, however, be measured at sufficient resolution to establish its identity.

### Methylglyoxal phosphorescence

The phosphorescence spectrum of methylglyoxal, excited by energy transfer from triplet  $\text{SO}_2$ , is reproduced in Fig. 2(a). The spectral slit width was 8 Å, and the total pressure in the flow tube 3 Torr. The band origin of the triplet spectrum of methylglyoxal is not known. Its position falls most probably between the band origins of glyoxal at 5208 Å [9], and of biacetyl at 5050 Å or 4920 Å (the latter is controversial [10, 11]; it does not coincide with the intensity maximum of biacetyl phosphorescence at 5125 Å, cf. Fig. 3). The structure of the methylglyoxal bands grouped around the

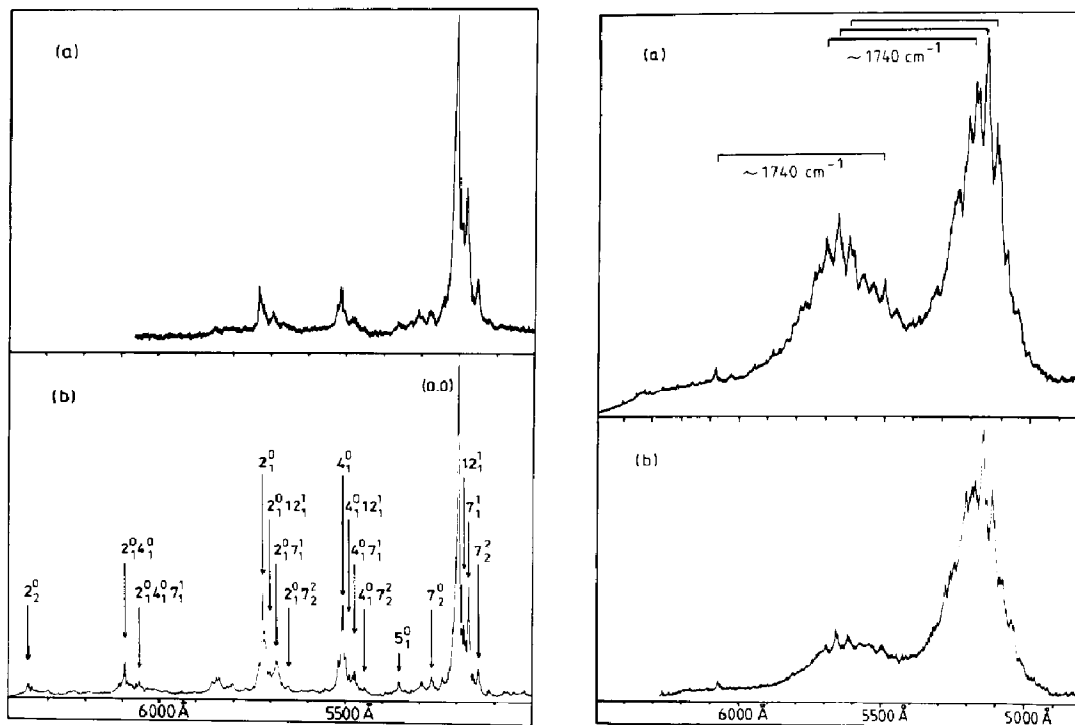


Fig. 1. (a) Glyoxal phosphorescence from the reaction of 6.8 Torr propene with 2 Torr ozonized oxygen; spectral slit width 8 Å. (b) Glyoxal phosphorescence excited by energy transfer from  $^3\text{SO}_2$  to glyoxal vapour at 3.2 Torr total pressure; spectral slit width 3 Å.

Fig. 2. (a) Methylglyoxal phosphorescence excited by energy transfer from  $^3\text{SO}_2$  to methylglyoxal vapour; spectral slit width 8 Å. (b) Methylglyoxal phosphorescence from the reaction of 4 Torr isobutene with 2.5 Torr ozonized oxygen; spectral slit width 6 Å.

most intense band at 5156 Å is repeated in a less intense band group shifted to the red by approximately  $1740\text{ cm}^{-1}$ , as indicated in Fig. 2. This wave-number comes close to the  $>\text{C}=\text{O}$  stretching vibrations in the ground states of glyoxal ( $1745\text{ cm}^{-1}$  [9]) and biacetyl ( $1734\text{ cm}^{-1}$  [12]), suggesting that a transition from the triplet state of methylglyoxal to the ground state of the molecule with one vibrational quantum in a  $>\text{C}=\text{O}$  stretching mode is responsible for the shifting. Figure 2(b) shows for comparison a chemiluminescence spectrum produced by the reaction of 4 Torr isobutene with 2.5 Torr ozonized oxygen. The spectral slit width was 6 Å. Differences in the overall intensity distribution of the two spectra are accounted for by the spectral response curves of the different detection systems. Otherwise the resolved structures of both spectra are identical (some blurring out of the structure near 5260 Å in Fig. 2(a) is attributed to a transient fluctuation of the phosphorescence intensity which was measured simultaneously through an interference filter). It has thus been established that the chemiluminescence from the reaction of ozonized oxygen with isobutene is due, in this wavelength range, to methylglyoxal phosphorescence, as previously proposed by Finlayson *et al.* [6]. Identical phosphorescence spectra at 6 Å resolution

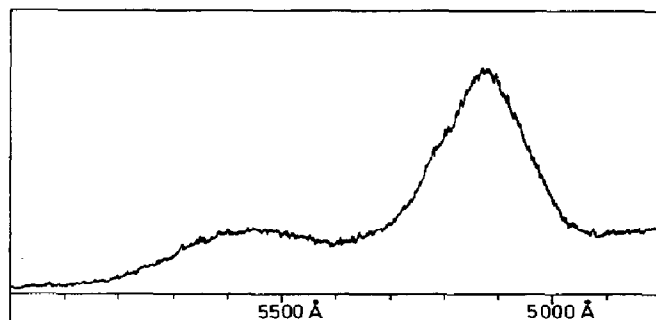


Fig. 3. Biacetyl phosphorescence excited by energy transfer from  $^3\text{SO}_2$  to biacetyl vapour at 2 Torr total pressure; spectral slit width 12 Å.

were obtained by the reactions of trimethyl- and tetramethyl-ethylene with ozonized oxygen.

#### *Biacetyl phosphorescence*

A phosphorescence spectrum of biacetyl, excited by the energy transfer method at 2 Torr total pressure at a low oxygen concentration in the flow tube, is reproduced in Fig. 3, at a spectral slit width of 12 Å. As would be expected, no vibrational structure could be resolved, also when the spectral slit width was reduced to 4 Å. The spectrum was needed for comparison with methylglyoxal phosphorescence from ozone-olefin reactions, to make a decision whether these were superimposed on biacetyl phosphorescence, as might be suspected. However, the ratios of peak height at 5156 Å to valley depth at 5136 Å were the same, within experimental accuracy, for the phosphorescence excited in methylglyoxal vapour (Fig. 2a) and for the chemiluminescence obtained with isobutene and tetramethyl-ethylene (Fig. 2b). We conclude that, contrary to earlier assumptions [5, 6], biacetyl does not contribute to the chemiluminescence of ozone-olefin reactions.

#### *Pressure dependence*

The intensity ratio of glyoxal phosphorescence to formaldehyde fluorescence in ozone-olefin reactions increases strongly with olefin pressure. The prominence of glyoxal phosphorescence in Fig. 1(a) is typical for high propene concentrations, whereas formaldehyde fluorescence dominates at lower concentrations [5]. We have evidence that this effect is not due to physical quenching of formaldehyde, but may be accounted for by a chemical reaction of a formaldehyde precursor with the hydrocarbon. The chemiluminescence spectra of isobutene and tetramethyl-ethylene, however, exhibit intense methylglyoxal phosphorescence also at extremely low concentrations of the olefins, and at high total pressures. This was established by means of the "inverted chemiluminescent ozone analyzer" at a total pressure of 400 Torr as follows: reactions of various olefins with excess ozone were studied at concentrations of only 500 p.p.b. olefin in synthetic air, measuring first the total chemiluminescence intensity  $I_{\text{tot}}$ , and then the par-

TABLE 1

Ratios  $I_{\text{tot}}/I_{\text{part}}$  of the total intensity  $I_{\text{tot}}$  and the partial intensity at wavelengths  $> 5000 \text{ \AA}$ , for the reactions of various olefins (500 p.p.b. in synthetic air) with ozonized oxygen at 400 Torr total pressure. The ratios are uncorrected for the spectral response of the bialkali photocathode

Olefin	$I_{\text{tot}}/I_{\text{part}}$
ethylene	12.0
propene	12.1
1-butene	10.0
<i>trans</i> -2-butene	13.3
1,3-butadiene	13.8
isobutene	2.5
tetramethyl-ethylene	2.6

tial intensity  $I_{\text{part}}$ , confined to wavelength  $\geq 5000 \text{ \AA}$  by a cut-off filter. Intensity ratios  $I_{\text{tot}}/I_{\text{part}}$ , uncorrected for the spectral response of the photocathode, are listed in Table 1. The olefins may thereafter be divided into two groups: the intensity ratios of propene, 1-butene, *trans*-2-butene, and 1,3-butadiene are comparable with ethylene, which gives rise to formaldehyde fluorescence, but not to glyoxal phosphorescence under any conditions. The chemiluminescence of isobutene and tetramethyl-ethylene, on the other hand, is characterized by an exceptionally low ratio of  $I_{\text{tot}}/I_{\text{part}}$  (which would be still further reduced if the spectral response of the bialkali photocathode were taken into account), indicating that methylglyoxal phosphorescence above  $5000 \text{ \AA}$  is very intense for these olefins.

This observation prompted us to measure the pressure dependence of methylglyoxal phosphorescence, using the  $5000 \text{ \AA}$  cut-off filter, 500 p.p.b. tetramethyl-ethylene in oxygen, and ozonized oxygen as reactants. The rate constant of this reaction is fast enough [2] that, by a proper choice of the flow rates, the reaction could be made to go to at least 99% completion within the reaction chamber at pressures of 20 Torr or less. A Stern-Volmer plot of  $1/I_{\text{part}}$  versus the total pressure is given in Fig. 4, which yields a slope/intercept ratio of  $0.17 \text{ Torr}^{-1} \pm 25\%$  for pure oxygen as pressurizing gas. Combining this value with the lifetime  $\tau = 1.92 \text{ ms}$  of triplet methylglyoxal [7] leads to a rate constant of  $k_{\text{q}}^{\text{O}_2} = 0.09 \text{ ms}^{-1} \text{ Torr}^{-1} \cong 2.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for its quenching by oxygen. This is substantially lower than the rate constant of  $3 \text{ ms}^{-1} \text{ Torr}^{-1}$  reported for the quenching of  $^3\text{A}_u$  glyoxal by oxygen [13]. A second experiment with 35% oxygen and 65% nitrogen as pressurizing gases yielded a slope/intercept ratio of  $0.075 \text{ Torr}^{-1} \pm 30\%$ , which gives a rate constant of  $0.008 \text{ ms}^{-1} \text{ Torr}^{-1} \cong 2.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the quenching of triplet methylglyoxal by nitrogen.

The relative importance of formaldehyde fluorescence, glyoxal phosphorescence, methylglyoxal phosphorescence, and possibly biacetyl phosphorescence, in ozone-olefin chemiluminescence spectra at higher pressures, may be inferred from the product of the collision-free lifetimes  $\tau$ , times the

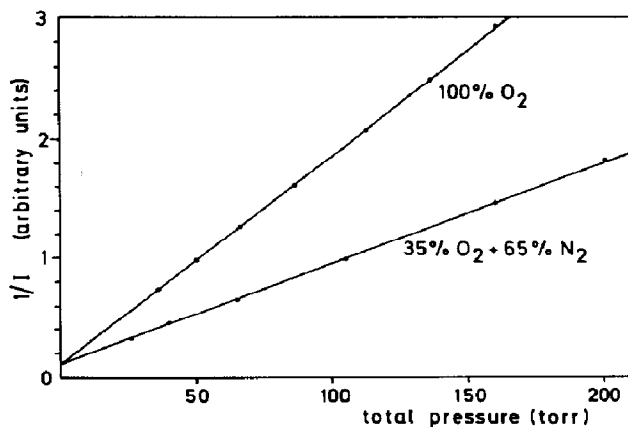


Fig. 4. Stern-Volmer plots of  $1/I_{\text{part}}$  (wavelengths  $>5000 \text{ \AA}$ ) vs. total pressure for the reaction of 500 p.p.b. tetramethyl-ethylene in oxygen, and in oxygen/nitrogen, with ozonized oxygen at constant mass flow rates.

quenching rate constants  $k_q^{\text{O}_2}$  of the four emitters, which yield Stern-Volmer slopes of  $2.8 \times 10^{-17}$ \*,  $3 \times 10^{-16}$  [13],  $5 \times 10^{-18}$  [7], and  $1.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1}$  [15, 16]. Glyoxal is clearly more sensitive to collisional quenching by oxygen than formaldehyde, whereas the intensity of methylglyoxal phosphorescence is expected to outrun formaldehyde fluorescence at high pressures. Biacetyl in its triplet state is most sensitive to quenching, making its detection rather improbable in systems containing several Torr oxygen.

#### Mechanisms of excited species formation

The mechanisms leading to electronically excited formaldehyde and  $\alpha$ -diketones have been discussed at length by Finlayson *et al.* [6]. There remains little doubt that most mechanisms, if not all, pass through dioxetane-like intermediates by intramolecular rearrangement processes. This assumption obtains further support from the recent observation of formaldehyde fluorescence from the addition of  $\text{O}_2(^1\Delta_g)$  to the double bond of ethyl vinyl ether at elevated temperatures [17], and the detection of substantial amounts of  $\alpha$ -diketones among the thermal decomposition products of certain dioxetanes.

A general rule can be derived from a comparison of olefins giving rise either to glyoxal phosphorescence or methylglyoxal phosphorescence: glyoxal phosphorescence is observed when one or two carbon atoms of the olefinic double bond bear a H atom and an alkyl group, as in propene and cyclobutene. Methylglyoxal phosphorescence arises when at least one carbon atom of the olefinic double bond bears two methyl groups, as in isobutene.

\* The collision-free lifetime  $\tau$  of vibrationally relaxed formaldehyde was taken as 282 ns, as measured by Yeung and Moore [14]. The rate constant  $k_q^{\text{O}_2}$  for its collisional quenching has not been measured; a value of  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was used as a reasonable estimate, to be compared with a rate constant of  $7.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for its self-quenching by  $\text{H}_2\text{CO}$  [14].

This simple rule suggests a common intramolecular re-arrangement mechanism of the primary ozone-olefin product to be operative, leading to excited  $\alpha$ -diketones. The involvement of a secondary reaction with molecular oxygen in the excitation mechanism of  $\alpha$ -diketones, proposed by Finlayson *et al.* [6], is ruled out by our observation that methylglyoxal phosphorescence is triggered by the reaction of isobutene with oxygen-free ozone, which was obtained by bubbling helium through a cold ozone solution in carbon tetrachloride.

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