

THE CHEMILUMINESCENT REACTION OF OZONE WITH KETENE

I. BARNES[†] and W. D. McGRATH*Department of Pure and Applied Chemistry, David Keir Building, The Queen's University of Belfast, Belfast BT9 5AG (U.K.)*

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Summary

The chemiluminescent emission resulting from the gas phase reaction between ketene and O₃ has been studied over the spectral region 280 - 520 nm. The most distinguishing features of the emission are identified as being due to electronically excited hydroxyl radicals (OH*), vibrationally excited hydroxyl radicals (OH[‡]) and electronically excited formaldehyde (HCHO*). The intensity of emission of all three species exhibited first-order dependence on the O₃ concentration and the peak intensities were compared with those obtained in the O₃-C₂H₄ system, studied under the same experimental conditions. The OH* and OH[‡] intensities were essentially the same in both systems whereas that of HCHO* was much greater in the O₃-CH₂CO system than for O₃-C₂H₄. The results are interpreted in terms of a mechanism involving formation, reaction and dissociation of the diradical CH₂O₂. This interpretation is shown to explain satisfactorily the results obtained from other systems involving reaction of O₃ with olefins and substituted ketenes.

In photochemical smog, O₃-olefin reactions constitute about 50% of the observed olefin degradation and this therefore makes them among the most important of the reactions in oxidative polluted atmospheres [1]. The products from these reactions are varied [2 - 5] and the vast majority show chemiluminescence of some description in the gas phase, the main excited species being electronically excited OH(²Σ⁺), HCHO(¹A''), CH(²Δ) and glyoxal (³A_u) and vibrationally excited OH[‡](X ²Π_{v<9}) [5 - 7].

The mechanism of gas phase ozonolysis is still not clearly defined. The Criegee mechanism involving a carbonyl and peroxy fragment [8] is normally used in conjunction with the O'Neal-Blumstein hydrogen abstraction modification [9] to account for the observed products and emissions. Even this combination of theories is not wholly satisfactory in explaining the diverse number of products, particularly the excited species, and the relative

[†]Present address: Fachbereich 9, Physikalische Chemie, Bergische Universität Wuppertal, 56 Wuppertal 1, F.R.G.

importance of each reaction mechanism has yet to be delineated. Methylene peroxide (CH_2O_2) is an important proposed intermediate in the Criegee mechanism for the ozonolysis of terminal olefins but which has yet to be experimentally synthesized or spectroscopically detected. Wadt and Goddard [10] in an extensive general valence bond–configuration interaction study on the geometry and molecular states of CH_2O_2 suggest that the further reactions of this species with O_3 etc. can satisfactorily explain all the observed excited species with the possible exception of $\text{OH}(^2\Sigma^+)$. Chemiluminescence has been observed in the $\text{O}_3\text{--CH}_2\text{CO}$ (ketene) reaction exactly analogous to that observed in the $\text{O}_3\text{--CH}_2\text{CH}_2$ reaction. Since CH_2CO has only one terminal CH_2 group, hydrogen abstraction reactions are severely limited and the observed emitting species can only be satisfactorily explained by the further reactions of CH_2O_2 and would seem to indicate support for the Wadt and Goddard proposal [10]. It may also possibly explain the formation of these emitting species in non-terminal olefins such as *cis*-2-butene since in these ozonolysis systems ketene is often a major product [4].

A simple flow tube consisting of a 15 cm length of Pyrex glass (25 mm outside diameter (OD) and 23 mm inside diameter (ID)) tapered at the pumping end and fitted with a 6 mm vacuum tap for coarse flow control was used for viewing the chemiluminescence. Two capillary inlets (6 mm OD and 4 mm ID) placed at right angles to each other and centred 2 cm from a quartz end-window delivered the respective reactant gases and ensured good mixing conditions. The light emitted from the flow tube was passed through a Bausch and Lomb single grating monochromator (33-86-02) set at a specific wavelength and detected with either a Hamamatsu R456 (UV–visible) or an R406 (S-1 spectral response) phototube, depending on the wavelength region under investigation.

The signal was then subsequently amplified by a factor of 100 using a Marconi preamplifier (TM6591A) powered by a 22 V battery supply and then passed to a signal averager, in this case a Princeton Applied Research (PAR) Boxcar integrator model 160 operated on an external trigger mode. A Grubb Parsons variable frequency chopping unit was used to drive a six-bladed chopper, operated at 850 Hz and positioned between the monochromator and the phototube, which supplied the triggering voltage. A reading at any wavelength setting took on average 10 min and these were taken at 5 nm intervals between 200 and 750 nm.

The typical total pressure in the flow tube for these experiments, measured by a Wallace and Tiernan absolute pressure gauge (0 - 20 Torr), was about 5 - 10 Torr; the partial pressures of O_3 and ketene were about 0.5 Torr and about 0.2 Torr respectively, the remainder being made up with either helium or nitrogen. Reactant mixtures were made up in 5 l bulbs and delivered to the flow tube via Edwards LB2B needle valves. The gas flow rates were measured with Monostat (36-541-07) flowmeters and varied between 10 and 80 $\text{cm}^3 \text{min}^{-1}$. O_3 was prepared by a silent discharge of 10 kV through oxygen using a Siemens ozonizer and was adsorbed onto pretreated silica gel maintained at -80°C from which it was desorbed and purified as

required. Ketene was prepared by the pyrolysis of acetone vapour on a red-hot tungsten wire. Free acetone, water and other condensable products were removed by a double-surface water-cooled condenser. The gas was then passed through two cold traps at $-35\text{ }^{\circ}\text{C}$ and finally condensed in a trap at liquid air temperatures. It was further purified by pumping under vacuum at $-196\text{ }^{\circ}\text{C}$ followed by vacuum distillation.

Since chemiluminescent experiments of the type described here can be strongly affected by slight traces of impurity, great care was taken to ensure that the ketene was as free from impurities as possible. The best conditions for ketene production were obtained using a flow rate of acetone vapour of $1\text{ cm}^3\text{ s}^{-1}$ and a tungsten wire temperature of $700\text{ }^{\circ}\text{C}$. This resulted in a 40% - 45% yield of ketene. The only other major products of the pyrolysis at this temperature are CH_4 , C_2H_6 , CO and C_2H_4 with trace quantities of ethyl methyl ketone. Vacuum distillation of the ketene was repeated until no traces of these impurities could be detected by IR and UV spectroscopy. It was of vital importance to remove C_2H_6 , CO and C_2H_4 traces, since these react with O_3 to give chemiluminescent emission, and the analytical procedure used ensured that impurities were not present above the detectable limit of 0.02 vol.%.

The chemiluminescent spectrum obtained for the reaction of O_3 with ketene is shown in Fig. 1, the partial pressures of the respective gases O_3 , CH_2CO and helium being 0.73 Torr, 0.18 Torr and 6.09 Torr. Similar chemiluminescence of an equal intensity was obtained with nitrogen as the added gas. The prominent features of the spectra are the $\text{OH}(^2\Sigma^+)$ emission at 310 nm and the banded $\text{HCHO}(^1\text{A}'')$ emission stretching from about 335 to 520 nm. A weak series of bands also extends from 595 to 695 nm (not illustrated) and it has been established with the use of a series of narrow bandpass filters that this emission extends as far as 900 nm. This emission is attributed to $\text{OH}(X^2\Pi_{v<9})$ (Meinel band emission [11]) as observed by various other workers in O_3 -olefin reactions [4 - 7]. For comparison, the chemilumi-

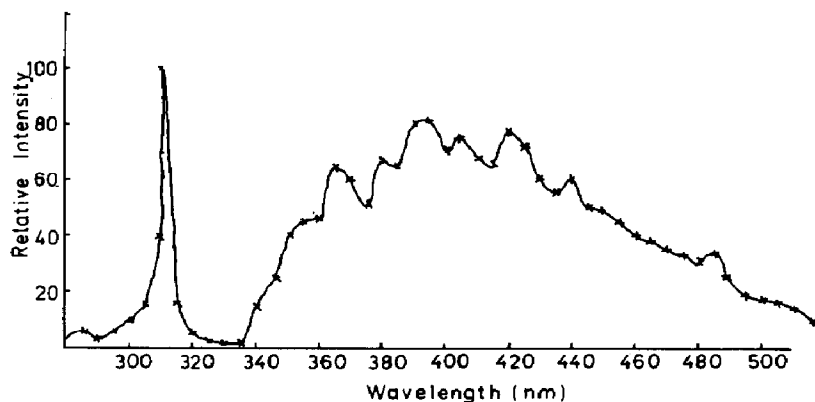


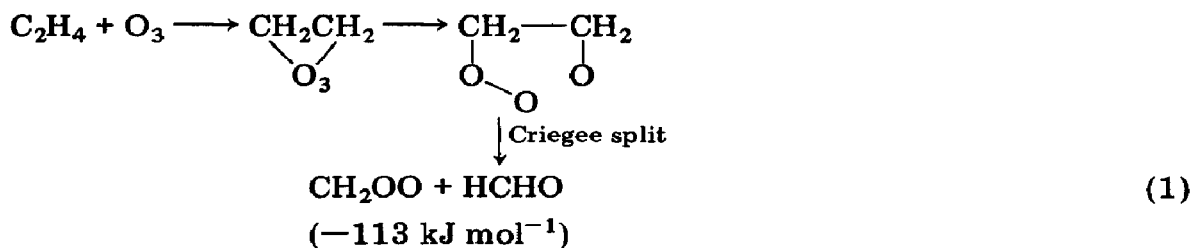
Fig. 1. Chemiluminescent emission observed from reaction between CH_2CO and O_3 . The relative intensities are normalized to 100 assigned to the peak of the $\text{OH}(^2\Sigma^+)$ emission (partial pressure of O_3 , 0.73 Torr; partial pressure of CH_2CO , 0.18 Torr; partial pressure of helium, 6.09 Torr; total cell pressure, 7.00 Torr).

nescence of the $O_3-C_2H_4$ reaction [5] was observed and was found to be similar in all respects to the O_3-CH_2CO chemiluminescence with the exception of a very weak emission from $HCHO(^1A'')$.

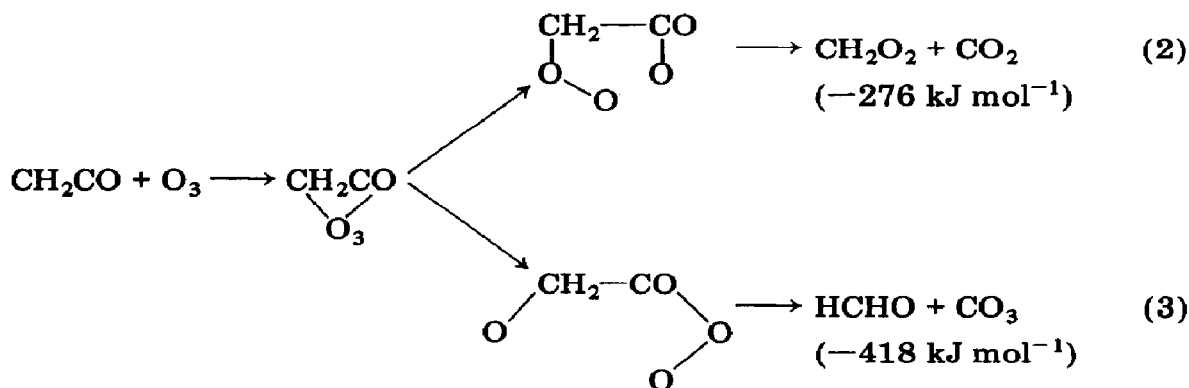
A comparison was made of the peak intensities for OH^* and OH^\ddagger emissions for the O_3-CH_2CO system with those for $O_3-C_2H_4$, under the same conditions of total pressure, flow rates and monitoring sensitivity. In the O_3-CH_2CO system the OH^* signal was 95% of that in the $O_3-C_2H_4$ system, whereas that of OH^\ddagger was the same in both. The $HCHO^*$ emission, however, was markedly different in the two systems. For O_3-CH_2CO its intensity was very much greater than that in the $O_3-C_2H_4$ system, being the same as that of OH^* , within the limits of experimental uncertainty. Under the experimental conditions used in these experiments the intensity of emission of all three species, OH^* , OH^\ddagger and $HCHO^*$, showed first-order dependence on the O_3 concentration.

The results show that all the emitting species associated with terminal olefin- O_3 reactions where both α - and β -hydrogen abstraction is possible can be obtained in the O_3-CH_2CO reaction where only α -hydrogen abstraction is possible.

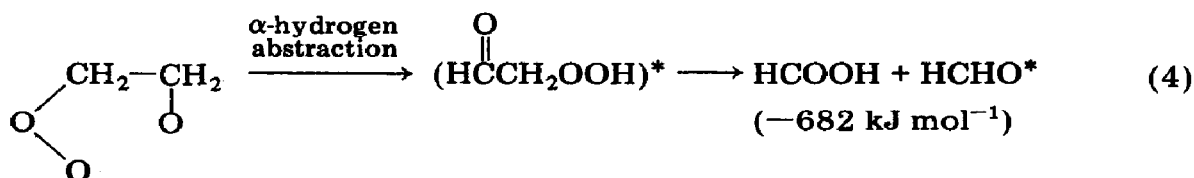
If it is assumed that the initial step in ozonolysis is the formation of a primary ozonide followed by rupture of an $O-O$ σ bond then, if the Criegee mechanism is followed, the reaction for C_2H_4 will be



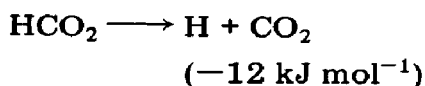
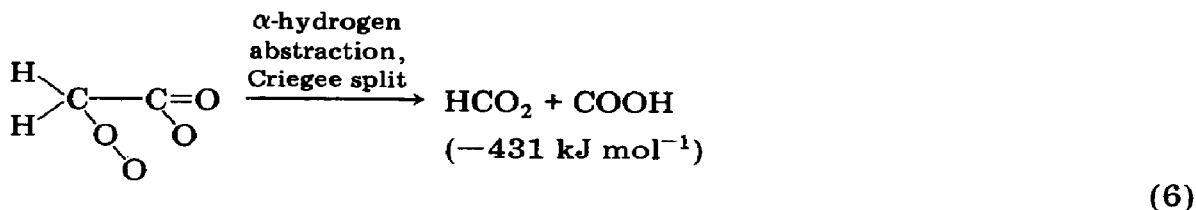
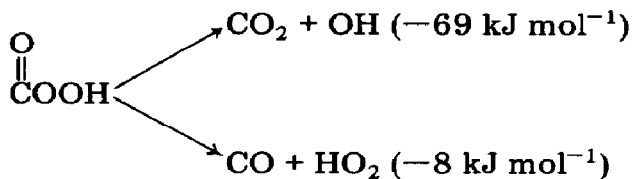
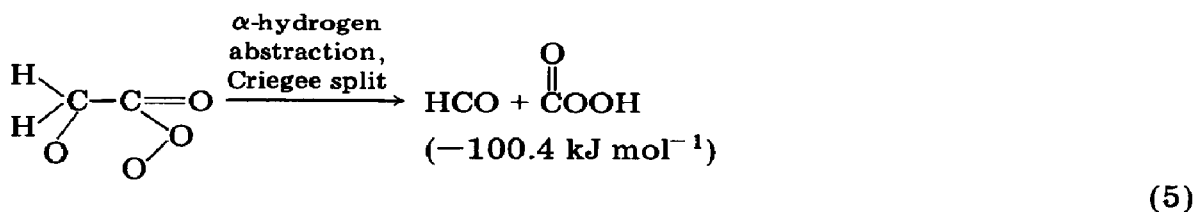
In the corresponding CH_2CO reaction two competing pathways are open:



The excitation energy for $\text{HCHO}(^1A'')$ is $337.2 \text{ kJ mol}^{-1}$ which means therefore that one of the Criegee splits (reaction (3)) in the $\text{O}_3\text{-CH}_2\text{CO}$ system is capable of directly producing this species but from analogy with other reactions of this type the possibility seems to be remote. Also there is no experimental or theoretical evidence to suggest that the exothermicity of reaction should be disproportionately distributed amongst the reaction products. The O'Neal-Blumstein modification of the Criegee mechanism involving α -hydrogen abstraction has been used to explain $\text{HCHO}(^1A'')$ formation in C_2H_4 ozonolysis [5], *e.g.*

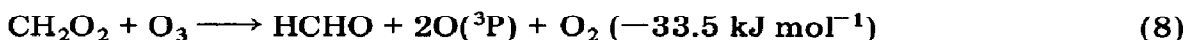
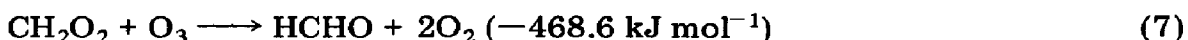


If the hydrogen abstraction is applied to the CH_2CO ozonolysis then two possible pathways exist:



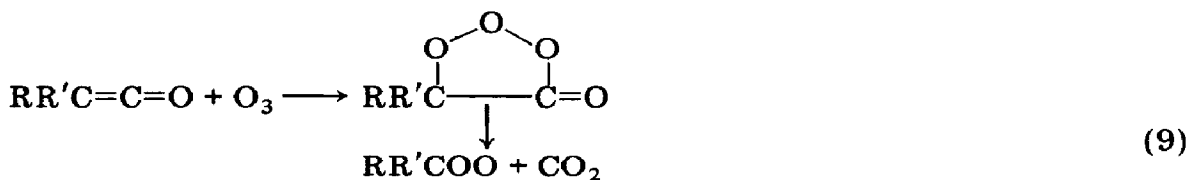
These two reaction pathways (5) and (6) can supply H, OH and HCO radicals, whose reactions with O, O_3 etc. are generally proposed to account for the formation of $\text{OH}(^2\Sigma^+)$ and $\text{OH}(X^2\Pi_{v<9})$ in these systems [10], but no $\text{HCHO}(^1A'')$. The formation of this species is more easily accounted for in

the O_3 - CH_2CO ozonolysis by the reaction of CH_2O_2 , formed via the Criegee split; with O_3 , two reactions are possible:



Reaction (7) is certainly capable of producing $HCHO(^1A'')$ and since the CH_2O_2 produced in the O_3 - CH_2CO reaction is much more likely to be either electronically or vibrationally excited than that formed in the O_3 - C_2H_4 reaction this may well explain the disparity in emission intensity of the species formed in the two systems. The further reactions of CH_2O_2 , rearrangement, unimolecular decomposition etc., can adequately account for all the other excited species [10], hydrogen abstraction being totally unnecessary at least for olefins containing a terminal $-CH_2$ group. Since CH_2CO is often a major product in the ozonolysis of more complex olefins not possessing terminal $-CH_2$ groups [4] it is possible that reaction (7) is still the dominant production path for $HCHO(^1A'')$ and subsequently the other excited species rather than the more complex hydrogen abstraction proposals [7, 9, 10] made for these reactions.

The recent work of Hatakeyama *et al.* [12] on the reactions of O_3 with ketene, methylketene, ethylketene and dimethylketene is of direct relevance to the previous discussion. They measured the reaction rates of these reactions but were only able to place an upper limit on the rate constant for the ketene- O_3 reaction of less than $1 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The rate constants for the other ketenes were more than a factor of 100 greater than this. These workers found that first-order decay behaviour for O_3 was not observed for conditions in which the concentration of O_3 was low and ketenes were present in excess, indicating the contribution of secondary reactions to the kinetics scheme which could not be inhibited, even when they added excess CH_3CHO to the systems, to act as a radical scavenger. In our experiments we found first-order dependence for the chemiluminescent emission for all emitting species under the experimental conditions described previously. In addition, for methylketene, ethylketene and dimethylketenes, when they used $^{18}O_3$ as reactant, the product CO_2 consisted mostly of $C^{16}O^{18}O$. They interpreted their results in terms of production of the biradical



followed by its decomposition, according to



They concluded that the biradical decomposes very quickly since even addition of a large excess of acetaldehyde failed to trap it. Our results are in agreement with these findings, apart from the fact that ours would indicate either a somewhat greater stability of CH_2O_2 in comparison with $\text{RR}'\text{CO}_2$ or a faster reaction rate of CH_2O_2 with ketene than that of $\text{RR}'\text{CO}_2$ with the higher ketenes.

In conclusion, it can be said that, although the O'Neal-Blumstein modified Criegee mechanism has been used to rationalize the formation of chemiluminescent species in gas phase O_3 -olefin reactions, it is found that this theory is not applicable to the observation of all the emitting species formed in the O_3 - CH_2CO reaction. These species are identical with those observed in the O_3 - C_2H_4 reaction and are better accounted for by the proposed role of CH_2O_2 as an intermediate. This inference supports the proposal of Wadt and Goddard [10] that electronically excited $\text{HCHO}(^1\text{A}'')$ is produced by the reaction of CH_2O_2 with O_3 (reaction (7)).

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