In conclusion we are convinced that the widely applicable chemistry of the Claisen rearrangement makes the homo-Claisen rearrangement and its concomitant possibilities important. We are currently investigating these questions.

Acknowledgment. We thank the National Institutes of Health (GM-29259) for financial support. We also thank Dr. Brian J. Willis (Fritzsche, Dodge and Olcott, New York) for a ^{13}C NMR spectrum of compound **7b**. NMR spectra were also obtained by using the 7 T spectrometer at The Rockefeller University purchased in part with funds from the National Science Foundation (PCM-7912083) and from the Camille and Henry Dreyfus Foundation.

Registry No. 4a, 80399-28-6; **4b**, 80399-29-7; **5a**, 80399-30-0; **5b**, 80399-31-1; **6a**, 80399-32-2; **6b**, 80399-33-3; **7a**, 80399-34-4; **7a** methyl ester, 80399-35-5; **7b**, 67279-65-6; **8**, 80399-36-6; **9a**, 80399-37-7; **9b**, 80399-38-8; **10a**, 80399-39-9; **10b**, 80399-40-2; **11a**, 80399-41-3; **11b**, 80399-42-4; **12**, 80399-43-5; **13**, 80399-44-6; **14**, 4111-01-7; TMSCH$_2$Cl, 2344-80-1; 2-butenal, 4170-30-3; 2-methyl-2-propenal, 78-85-3.

Single-Collision Chemiluminescent Reactions of Ozone with Hydrogen Sulfide and Methyl Mercaptan

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The reactions of ozone with a wide range of molecules have provided insight into many novel chemical processes. Ozonolysis of olefins is, of course, extremely important synthetically,[1] while reactions of ozone with metal atoms, M, yield information about the refractory MO species via chemiluminescence.[2] The reaction of O_3 with certain small molecules, e.g., NO,[3] is known to produce electronically excited products that can fluoresce on a single collision. Other molecules such as olefins and small sulfur-containing compounds react with ozone to produce chemiluminescent products possibly via multistep pathways.[4-6] We are interested in the dynamics of reactions of ozone with various organic molecules and began our studies with mercaptans.[7] We have previously studied the reaction of ozone with H_2S and CH_3SH to produce electronically excited SO_2. This work was carried out at low pressures but still under multiple-collision conditions. In this communication, we present single-collision studies[8] of the chemiluminescent reactions of ozone with H_2S and CH_3SH.

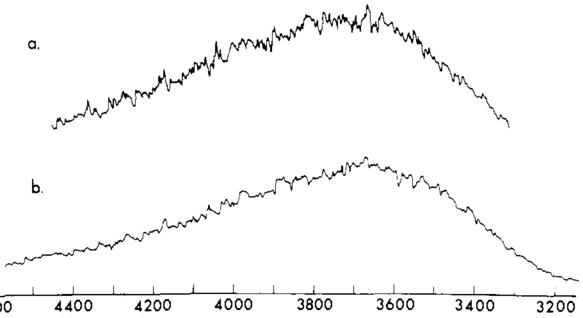

Figure 1. Continuous chemiluminescence spectra of SO_2 from ozone reactions under multiple-collision conditions. The short wavelength cutoff is due to the Pyrex window. (a) Chemiluminescence spectrum recorded from the reaction of 10-μm O_3 (beam) with 5-μm CH_3SH. (b) Chemiluminescence spectrum recorded from the reaction of 40-μm O_3 (beam) with 10-μm H_2S; 1 μm = 10^{-3} torr.

The reactions were studied in our beam-gas chemiluminescence apparatus which has been previously described.[7] Briefly, an evacuated chamber (base system pressure $<1 \times 10^{-6}$ torr) is filled to a certain pressure with a background gas. A molecular beam of ozone is injected into the chamber, and the ozone molecules undergo collisions with the background gas. Due to the large exoergicity of the reactions, products can be generated in electronically excited states. These molecules can fluoresce, and the emitted photons are detected perpendicular to the beam axis through a Pyrex viewing window.[9] The photons are spectroscopically analyzed by using an 0.75-m Spex monochromator and are detected by a cooled photomultiplier tube (EMI 6256 B). Due to the low cross section for photon production, photon-counting techniques must be employed. The output of the photomultiplier tube was sent to an Ortec pulse counting system. The pressure was determined by an ion gauge for pressures $<10^{-3}$ torr and by a Granville–Phillips Convectron gauge for pressures $>10^{-3}$ torr. These measurements should be accurate to 50%. Ozone, produced in a commercial ozonizer, was collected on silica gel at −59 °C. The ozone container was flushed with helium to eliminate as much O_2 as possible and then warmed gradually to room temperature. The background reagent gases, H_2S and CH_3SH, were obtained from commercial sources and were used without further purification.

The continuous spectra obtained for $O_3 + CH_3SH$ and $O_3 + H_2S$ under multiple-collision conditions are shown in Figure 1, a and b, respectively. This spectrum corresponds to the fluorescent spectrum of SO_2 and is essentially identical with that recorded by Halsted and Thrush[10] from the reaction

$$SO + O_3 \rightarrow SO_2 + O_2 \qquad (1)$$

and with the low-pressure luminescent spectrum obtained by Strickler et al.[11] Due to the complicated manifold of electronic states for SO_2, the individual vibrational lines have not been resolved.[12] In figure 2, a and b, we show the digital spectra obtained for the reaction of O_3 with H_2S and O_3 with CH_3SH at very low pressures. At this pressure (4×10^{-4} torr), the mean free path is on the order of 10 cm; within the region viewed by the monochromator, this corresponds to single-collision conditions. The bar spectra follow the general shape seen in the higher pressure spectra, and we attribute the spectra to SO_2. A digital spectrum obtained at a pressure of 6×10^{-5} torr (definitely in the single-collision regime) is shown in Figure 2c for the reaction of H_2S. It is again similar to the higher pressure spectra. In another

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[‡] Alfred P. Sloan Foundation Fellow (1977–1981); Camille and Henry Dreyfus Teacher–Scholar (1978–1983); DuPont Young Faculty Grantee (1978).

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(8) The mean free path, *l*, for various pressures based on a cross section of 3.7 Å^2: $P = 1 \times 10^{-5}$ torr, $l = 500$ cm; $P = 5 \times 10^{-5}$ torr, $l = 100$ cm; $P = 1 \times 10^{-4}$ torr, $l = 50$ cm; $P = 5 \times 10^{-4}$ torr, $l = 10$ cm. The single-collision regime occurs when *l* is greater than the dimensions of the apparatus. In this case the chamber is a cylinder ($r = 18$ cm × $L = 60$ cm).

(9) The Pyrex window imposes a short wavelength cutoff of ~3300 Å.

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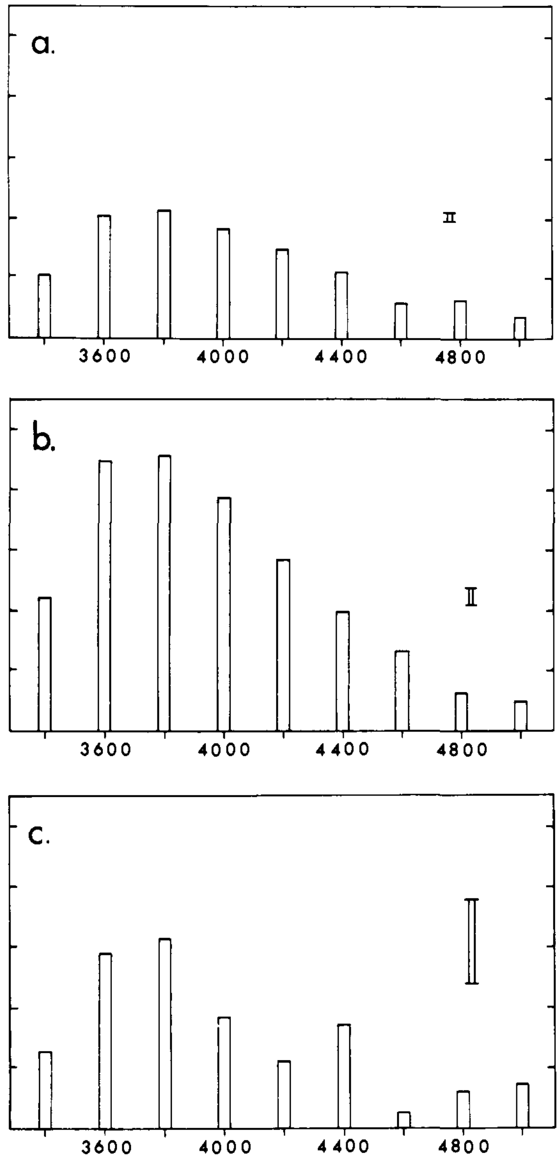


Figure 2. Digital chemiluminescence spectra of SO_2 from ozone reactions under single-collision conditions. (a) Chemiluminescence spectrum from the reaction of 0.2-μm O_3 (beam) with 0.2-μm CH_3SH. (b) Chemiluminescence spectrum from the reaction of 0.2 μm O_3 (beam) with 0.2-μm H_2S. (c) Chemiluminescence spectrum from the reaction of 0.03-μm O_3 (beam) with 0.03-μm H_2S; 1 μm = 10^{-3} torr.

experiment, we found that the contour is reproduced at a total pressure of 2×10^{-5} torr. In order to further demonstrate that the reaction was proceeding under single-collision conditions, the intensity of a single line (3800 Å) was measured as a function of the background gas pressure while keeping the beam pressure constant. This plot is shown in Figure 3. The signal is observed to increase linearly with pressure, demonstrating a 1:1 correspondence between the luminescent species and the reagent gas. At pressures above 1×10^{-4} torr (higher signal) and below 5×10^{-4} torr, a linear dependence of signal with increasing pressure is found with much smaller scatter in the points. Furthermore, the very low pressures employed in this study ($<10^{-4}$ torr) guarantee that the signal observed is from a species formed in a single collision.

The only possible reactions that can yield SO_2^* in a single collision are

$$O_3 + H_2S \rightarrow SO_2 + H_2O \qquad (2)$$

$$O_3 + CH_3SH \rightarrow SO_2 + CH_3OH. \qquad (3)$$

The reactions as written are exothermic by −158 and −146 kcal/mol, respectively.[13] The production of luminescence at the highest energy light observed (due to the cutoff of our Pyrex window) is around 85 kcal/mol. The remaining energy for reactions 2 and 3 is not sufficient to dissociate any of the bonds in the product, so these are the only single-collision reactions that can energetically produce SO_2 in an excited state.

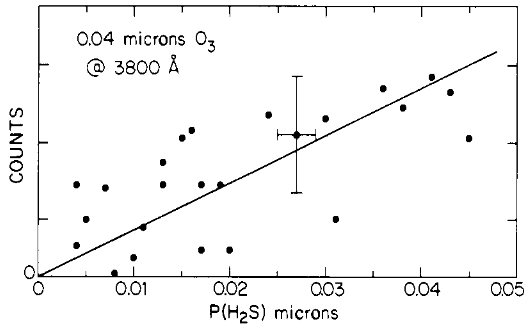


Figure 3. Dependence of the chemiluminescence intensity at 3800 Å on the pressure of the H_2S background reagent gas for the reaction of O_3 with H_2S. The O_3 was injected as a beam at a pressure of 0.04 μm (4×10^{-5} torr).

Table I. Relative Cross Sections for SO_2^* Chemiluminescence

P,[a] μm	I_{CH_3SH}/I_{H_2S}
1000	80[b]
40	3[c]
1	0.8[c]
0.06	0.5[c]

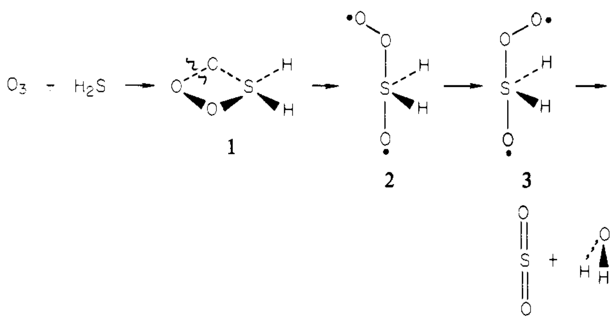
[a] Total pressure in microns (10^{-3} torr). [b] Reference 5a–c. [c] These values are accurate to ±25%.

In order to examine emission in the ultraviolet to provide further evidence for these reactions, we added a quartz window to our system. If the emission is due to the multistep mechanism, the precursor reaction is considered to be

$$SO + O_3 \rightarrow SO_2^* + O_2 \qquad (4)$$

with an exoergicity of 106 kcal/mol. The minimum wavelength of light that can be observed due to reaction 4 is 2700 Å. For low-pressure mixtures of H_2S and O_3, emission at wavelengths shorter than 2700 Å can only come from reaction 2. We have observed chemiluminescence down to 2500 Å (114-kcal/mol exothermicity). This emission is very difficult to observe since the cross section is low and due to the possibility of "ghost" effects in the monochromator from the more intense longer wavelength emission. Careful checks of our results showed that the emission is due to photons with λ = 2500 Å and comes from the single-collision reaction of O_3 with H_2S.

The remarkable result is the amount of atomic rearrangement that occurs in these reactions. We envision the following mechanism for the reaction of H_2S with ozone based on analogous chemistry in olefins.[14] The ozone adds to the sulfur to form a hypervalent species (**1**), and subsequently an O–O bond breaks



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to form a species **2** with a structure similar to that of SF_4.[15] The "dangling" oxygen then rotates over the two hydrogens (**3**), and separation to the products H_2O and SO_2 occurs. A similar mechanism can be realized for the mercaptan reaction.

The ratio of cross sections for the production of chemiluminescence from the CH_3SH and H_2S reactions with ozone has been measured over more than four orders of magnitude in pressure, and the results are shown in Table I.[16] At high pressures (multiple-collision conditions), the intensity of the light produced by the mercaptan reaction is almost two orders of magnitude greater than that produced by H_2S. As the pressure decreases, the intensities approach a ratio of 1. In the single-collision regime, the intensity from the H_2S reaction is greater than that for the CH_3SH reaction by a factor of 2. This shows a change in the dominant mechanism for producing the luminescence that is strongly pressure dependent. In the single-collision regime the reaction of H_2S with ozone is more efficient at producing light. As the pressure increases into the multiple-collision regime, a chain mechanism becomes the dominant means for producing luminescence. The chain mechanism is more efficient in the case of the mercaptan than in the case of the sulfide.

We are pursuing further studies of these reactions and those of other sulfur containing compounds in order to provide further information about the dynamics of these reactions and the spectroscopy of SO_2.

Acknowledgment. This research was supported in part by the National Science Foundation Grant CHE-7905985. We thank Professor S. Lipsky for loaning us the pulse-counting system.

Registry No. O_3, 10028-15-6; H_2S, 7783-06-4; CH_3SH, 74-93-1; SO_2, 7446-09-5.

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[16] An estimate of the cross section for the production of chemiluminescence in reaction 2 is 1×10^{-5} Å^2.

Elimination-Addition Mechanisms of Sulfonyl Group Transfer: Evidence for a Sulfoquinone Intermediate in the Hydrolysis of 2,4-Dinitrophenyl 3,5-Dimethyl-4-hydroxybenzenesulfonate[1]

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We report here the first definitive evidence for the participation of a dissociative (EA)[2] mechanism in the basic hydrolysis of a 4-hydroxybenzenesulfonic acid ester, namely, 2,4-dinitrophenyl 3,5-dimethyl-4-hydroxybenzenesulfonate (**1**).[3]

Reaction rates were measured by following spectrophotometrically the formation of the phenolate ion, which was released quantitatively in every case. Pseudo-first-order rate constants were found to depend on pH according to eq 1, and the sigmoidal log

$$k_{\text{obsd}} = k'/(1 + a_{\text{H}}/K_{\text{a}}) \qquad (1)$$

k_{obsd} vs. pH profile is shown in Figure 1. In the pH range 9–13.5, the k_{obsd} values are essentially constant and equal to k' (3.18×10^{-3} s^{-1}) and the inflection corresponds to pK_{a} = 7.4, identical in value (within the experimental error) with the apparent pK_{a} determined spectrophotometrically under identical conditions.

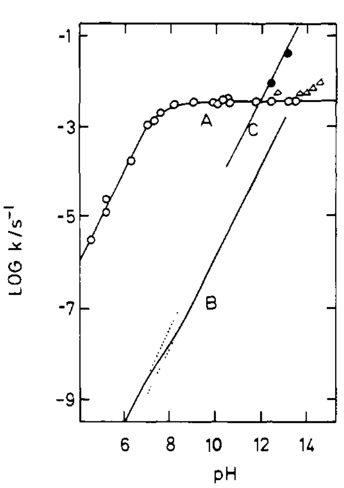
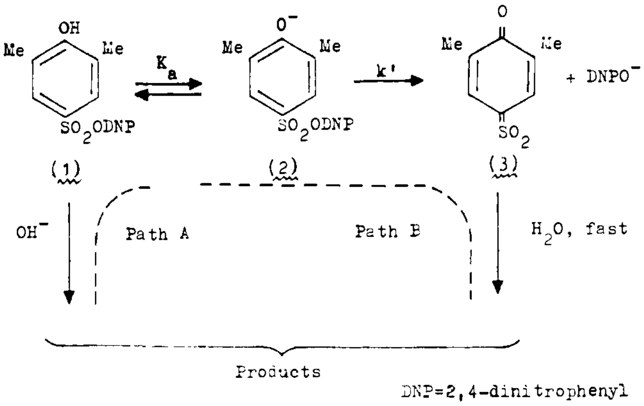


Figure 1. Dependence on pH of the hydrolysis of 2,4-dinitrophenyl 3,5-dimethyl-4-hydroxybenzenesulfonate (20% dioxane/water (v/v), 25 °C, ionic strength made up to 0.2 M (○) or 1 M (△). (A) Theoretical, from data in the text and eq 1; (B) calculated reactivity of the ester hydrolyzing through a normal BAc2 mechanism (see text); dotted lines are to accentuate the inflexion at the pK; (C) 2,4-dinitrophenyl benzenesulfonate. The kinetic results are extrapolated to zero buffer concentration.

Scheme I



The observed dependence of rate on pH could be attributed either to an associative (AE)[2] mechanism in which nucleophilic attack of the hydroxide ion on the substrate **1** is inhibited as the latter undergoes ionization (path A in Scheme I) or to a dissociative (EA) mechanism where the limiting rate k' represents the unimolecular breakdown of the substrate conjugate base **2**.

We can calculate to a good approximation the nucleophilic reactivity of the hydroxide ion toward esters **1** and **2** as expressed by the second-order rate constants ($k_{\text{OH}}^{\text{calcd}}$) on the basis of the known reactivity of 2,4-dinitrophenyl benzenesulfonate[4] and the sensitivity of the reaction to substituents in the acid moiety (ρ 2.24).[5] The second-order rate constant $k_{\text{OH}} = k'K_{\text{a}}/K_{\text{w}}$ for the bimolecular reaction of ester **1** with the hydroxide ion, calculated from the experimental values of k' and K_{a} and the reported value[6] of K_{w} for the mixed solvent used, is some 5×10^5-fold larger than the $k_{\text{OH}}^{\text{calcd}}$ value for the same ester. Such a very large reactivity ratio is considered as good evidence in favor of different mechanisms operating in the reactions under comparison,[7] and we conclude that only the dissociative mechanism is operating. It is most likely that the unsaturated intermediate involved in the EA route is the sulfoquinone species **3** (path B). If the mechanism

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[1] We are grateful to NATO (Grant RG 115.80) for partial financial support of this research.

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