for the ortho isomer. Although both isomers suffer about the same change in acidity in going from S_0 to S_1 , the meta isomer is a weaker acid than the ortho isomer in the S_1 state because it is a weaker acid in the ground state. Although the para isomer is a stronger acid than the meta isomer in the ground state, the change in acidity produced by going from the S_0 to the S_1 state is such that the meta isomer is the stronger acid in the S_1 state.

Interestingly, the triplet-state dissociation constants, pK_T , follow the same order as the pK_{S_1} values, ortho < meta < para. In this case also, $pK_{S_0} - pK_T$ is almost identical for the ortho and meta isomers and smallest for the para isomer. As is usually the case, $pK_{S_1} < pK_T < pK_{S_0}$ 9). It has been accepted for a long time that phosphorescences arising from ${}^3\pi,\pi^*$ states of aromatic molecules, even benzenoid compounds, invariably originate from the 3L_a state.^{12,13} However, this would dictate the order para > meta \approx ortho for $pK_{S_0} - pK_T$ and para < ortho < meta for the pK_T values. The results of the experiments given here (Table II) indicate that the order of

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 pK_T (and of $pK_{S_0} - pK_T$) is identical with that of pK_{S_1} (and of $pK_{S_0} - pK_{S_1}$) and strongly suggest that phosphorescence originates from the ³L_b state in the cyanophenols.

The assignment of the lowest triplet state of aromatic molecules to the L_a term is largely based upon the relatively constant ratio (~1.7) of the frequency of the ${}^{1}L_{a}$ band to that of the lowest-frequency singlet-triplet absorption band (t band) in aromatic hydrocarbons.¹⁴ In the cyanophenols the ratio of the frequencies of the ${}^{1}L_{a}$ and phosphorescence bands gives a ratio of 1.6-1.8 for the ortho and meta isomers and 1.4-1.6 for the two species derived from the para isomer. On the other hand, the ratio of the frequencies of the ¹L_b and phosphorescence bands ranges between 1.3 and 1.4 for all species derived from all of the cyanophenols. Consequently, if the consistency of the relationship between the frequency of a given singlet-singlet transition and a singlet-triplet transition, over a series of molecules, is to be taken as evidence of similarity between the in-plane polarization characteristics of the transition, the phosphorescences of the cyanophenols must be assumed to originate from the ${}^{3}L_{b}$ state.

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Emission from FCO in the Reactions of Ozone with Fluoroethenes

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The gas-phase reactions of ozone with cis-1,2-difluoroethene, trans-1,2-difluoroethene, trifluoroethene, and chlorotrifluoroethene are all accompanied by light with a maximum intensity at approximately 425 nm. A partial vibrational analysis of this emission is presented and it is concluded that the emitting species is the FCO radical, as previously suggested. A comparison is made between the enthalpy changes of the primary reactions between ozone and the fluoroethenes and their correlation with the identity of the emitting species. The exothermicity of the reaction correlates with the chemiluminescent reaction channel.

The reactions of ozone with alkenes are important in the environment and have provided a rich source of kinetic and spectroscopic data. Pitts and co-workers have identified HCHO (¹A''), OH(X²\Pi, $v \leq 9$) and OH(A²Σ⁺) in the chemiluminescent reaction of O₃ with ethylene.^{1,2} We have noted^{3,4} an emission with a maximum at approximately 425 nm in the reaction of O₃ with *cis*-1,2-C₂H₂F₂, *trans*-1,2-C₂H₂F₂, C₂HF₃, and C₂ClF₃. Pitts et al. have also reported this emission² and tentatively ascribed it to the FCO radical. We now give a partial vibrational analysis which confirms Pitts' suggestion and we also consider the relationship between the exothermicity and chemiluminescence of the reaction of O₃ with fluoroethenes.

The apparatus was similar to that previously described.^{3,5} Ozone was prepared by passing oxygen (Matheson Ultrapure Grade) through an ozonizer operated at 7.5 kV and trapping the O_3 in silica gel at -78 °C. The

TABLE I:	Deslandres	Table	of FCO	Band	(cm ⁻¹)
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	ν, ''						
v 2 ''	0	0		1			
0							
1			27586				
			632				
2			26954	912	26042		
			509		661		
3			26455	1074	25381		
			658		629		
4	26810	1103	25707	955	24752		
	700		644		656		
5	26110	1047	25063	967	24096		
	502		613		622		
6	25608	1158	24450	976	23474		
	670		584		647		
7	24938	1072	23866	1139	22727		
	715		610		554		
8	24242	986	23256	1083	22173		
_	489		632				
9	23753	1139	22624				
	712		646				
10	23041	1063	21978				

silica gel trap was then evacuated to remove adsorbed O_2 until appreciable quantities of O_3 desorbed, and the trap was then allowed to warm to room temperature, allowing

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TABLE II: Primary Pathways for Reactions of Ozone with Ethylenes

reaction	identified emitters	ref	$\Delta H^{\circ},$ kcal/mol
$O_3 + C_2H_4 \xrightarrow{1} HCHO + HCOOH$	HCHO*	1, 2	-163
$O_3 + C_2H_3F \xrightarrow{2a} HCOF + HCOOH$			183
$\frac{2\mathbf{b}}{\mathbf{b}}$ HCHO + FCO + OH			- 60
$\xrightarrow{2c}$ HCHO + CHF + O ₂			+11
$O_3 + 1, 1 - C_2 H_2 F_2 \xrightarrow{3a} COF_2 + HCOOH$			-199
$\frac{3b}{100}$ HCHO + CF ₂ + O ₂			- 27
$O_3 + 1,2-C_2H_2F_2 \xrightarrow{4a} HCOF + FCO + OH$	FCO*	2, 3, 4	-78
$\frac{4b}{2}$ HCOF + CHF + O ₂			- 8
$O_3 + C_2 HF_3 \xrightarrow{5a} COF_2 + FCO + OH$	FCO*	4	-104
$\frac{5b}{100}$ COF ₂ + CFH + O ₂			-33
$\frac{5c}{100}$ HCOF + CF ₂ + O ₂	CF ₂ *		- 55
$O_3 + C_2 ClF_3 \xrightarrow{6a} COF_2 + FCO + ClO$	FCO*	4	- 76
$\frac{6 b}{COF_2} + CClF + O_2$			-52
$\frac{6c}{100} \text{COClF} + \text{CF}_2 + \text{O}_2$			- 54
$O_3 + C_2F_4 \xrightarrow{7} COF_2 + CF_2 + O_2$	CF ₂ *	3	-73

the O_3 helium. In some cases the O_3 was eluted directly from the warmed silica gel trap with a stream of helium. Total pressures were generally ~ 50 torr with typical partial pressures of 0.2 torr of O_3 and 1 torr of substrate.

Commercial fluoroethenes were vacuum distilled before use with liberal rejection of head and tail fractions. The reaction vessel was approximately 65 cm long and substrates were mixed with O_3 60 cm from the monochromator inlet. A Jarrell-Ash 0.25-m monochromator with a 2360 groove/mm grating and a 3-nm spectral slit width viewed the reaction vessel axially through a quartz window. A cooled EMI 9683QKB photomultiplier was used.

Results and Discussion

Similar spectra of comparable intensity and with maxima at 425 nm were obtained with cis-1,2- $C_2H_2F_2$, trans- $1,2-C_2H_2F_2$, and C_2HF_3 . In the latter case, additional maxima at 320 and 560 nm were seen and may be attributed to $CF_2({}^{1}B_1)$ and $CF_2({}^{3}B_1)$, respectively.⁵ The most intense spectrum was obtained with C_2ClF_3 and this is shown in Figure 1.

The absorption spectrum of FCO has been reported by Jacox et al. in condensed phases^{6,7} and by Wang and Jones in the gas phase⁸ but not hitherto in gas-phase emission. A vibrational analysis of the 425-nm band was carried out using the published fundamental frequencies⁷ for $\nu_1(CO)$ stretch) = 1857.0 cm⁻¹, ν_2 (bend) = 627.5 cm⁻¹, and ν_3 (CF stretch) = 1023.0 cm⁻¹, and a Deslandres table is shown in Table I. The 000 emission band was assumed to lie at 341 nm, a shift of 120 cm⁻¹ to the blue from the matrix assignment.^{7,8} Three distinct progressions could be assigned in the bending mode and the CF stretch. These are shown as $000 \rightarrow 0\nu_2^{\prime\prime}0, 000 \rightarrow 0\nu_2^{\prime\prime}1$, and $000 \rightarrow 0\nu_2^{\prime\prime}2$ in Figure 1 and Table I. Frequency differences are in accord with those obtained for the absorption spectrum and we conclude that the 425-nm band seen in the reactions of O_3 with cis-1,2- $C_2H_2F_2$, trans-1,2- $C_2H_2F_2$, C_2HF_3 ,



Figure 1. Emission from the reaction of ozone with chlorotrifluoroethene. Vibrational assignments are for FCO emission.

Scheme I



and C_2ClF_3 is due to the electronically excited FCO radical.

The relationship between thermochemistry and reaction mechanism in the ozone-alkene reactions is extremely complex and it has been discussed in detail by Nangia and Benson.⁹ We consider here the compatibility of the chemiluminescence for some known emitters with the enthalpy of the reactions.

The Criegee mechanism for ozonolysis in the liquid phase is also valid in the gas phase⁹ although biradicals

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rather than Zwitterions are probably formed.¹⁰ We may then write a simplified scheme for the fluoroethenes (Scheme I). The primary products are an aldehyde and an unstable peroxide which may decompose or, in the case of $R_1 = R_2 = H$, rearrange to form vibrationally excited formic acid. We have listed the reaction pathways for the ozonolysis of fluorethenes and these are given in Table II with the corresponding enthalpies of reaction in the Appendix¹¹ and identified electronically excited emitters. We have omitted the many secondary reactions, such as the decomposition of excited formic acid.¹²

The possible precursors of the very weak emission which accompanies the C_2H_3F and $1,1-C_2H_2F_2$ reactions are also omitted from Table II. These two reactions (listed as reactions 2 and 3 in Table II) are not yet sufficiently understood for comparisons with exothermicity to be useful. We have found¹³ a very weak luminescence from the reaction of O_3 with C_2H_3F with a maximum at 440 ± 20 nm. Product analysis for this reaction in the liquid phase has shown that both CH₂O₂ and CHFO₂ intermediates are involved.¹⁴ The reaction of O_3 with $1,1-C_2H_2F_2$ also emits weakly,^{2,3} but more work needs to be done before the emitter can be indentified. The other reactions in Table II show that when there is more than one pathway for the decomposition of a peroxy radical, the luminescence accompanies the more exothermic channel. Thus reaction 4a is preferred over (4b) and (5a) is preferred over (5b). Reaction 5c occurs because of the channel involving the CF_2O_2 intermediate. Reaction 6a is preferred over (6b) but emission from (6c), analogous to (5c), does not seem to occur. This could be due to the fact that the triplet energy of CF_2 , barely reached in reaction 5c, is not attained in (6c). It should be noted that the uncertainty in ΔH° for reaction 6c is about $\pm 8 \text{ kcal/mol.}^{11}$

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Appendix. Thermochemical Data

Exothermicities were calculated from the following values of $\Delta H_{\rm f}^{\circ}$ (298 K, gas-phase) in kcal mol⁻¹: O₃, 34.1;^{15a} OH, 9.3;^{15a} ClO, 24.5;^{15a} CF₂, -44.6;^{15b} CHF, 39 ± 4 ;^{15c} CClF, 7;^{15d} FCO, -41 \pm 15;^{15e} COClF, -102 \pm 8;^{15e} HCOF, -90;^{15e} ., 1.00, 41 \pm 15, 10, 100 \pm 8, 102 \pm 8, 106 HCOF, -90; 166 COF₂, -152.0; 15e HCHO, -25.9; 15a HCOOH, -90.5; 15f C₂H₄, 12.5; 15a C₂H₃F, -31.6; 15f 1, 1-C₂H₂F₂, -77.5; 15g cis- or trans-1, 2-C₂H₂F₂, -77; 15d C₂HF₃, -114; 15g C₂F₄, -157.4; 15e C₂ClF₃, -127.15g

The ¹⁴N and ²H Nuclear Quadrupole Resonance Spectra of Anthranilic Acid

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The ¹⁴N quadrupole resonance spectra have been obtained at 77 K for all three polymorphic forms of anthranilic acid (o-aminobenzoic acid). In addition, ²H spectra were obtained for forms I and II in which the exchangeable hydrogens were replaced by deuterium. It was not possible to obtain a sample of deuterated form III. In form I, nonequivalent nitrogens with $e^2 Qq_{zz}/h$ values of 1602 and 2999 kHz were observed. These correspond to the nitrogens of the zwitterionic and neutral molecules, respectively. Forms II and III give rise to only one type of nitrogen each, with $e^2 Qq_{zz}/h$ values of 3607 and 3705 kHz, respectively. The NQR observations are entirely consistent with previous X-ray studies of the polymorphs. The ²H NQR spectra are complex due to the presence of nonequivalent deuteriums which are dipolar-coupled. In form I the ND_3^+ group gives rise to e^2Qq_{zz}/h values of 130.2, 143.4 and 155.3 kHz, respectively. For the ND₂ groups of this polymorph, the values are 203.2 and 212.4 kHz, respectively. Form II yields deuterium quadrupole coupling constant values for the -ND₂ group of 227.1 and 229.8 kHz, respectively. The O-D groups in forms I and II give rise to quadrupole coupling constants of 184.0 and 172.2 kHz, respectively. The O-D groups in forms I and II give rise to quadrupole coupling constants of 184.0 and 172.2 kHz, respectively. In the deuterated solids satellite lines are seen on the ¹⁴N transitions, as a result of simultaneous spin flips of the ¹⁴N and directly bound ²H. These lines are of help in assigning the complex spectra in the region of the pure ²H transitions, where dipolar coupling of closely located, slightly nonequivalent dueteriums gives rise to a multiplet structure. Several examples of double transitions, involving simultaneous spin flips of deuteriums, are also reported. The deuterium quadrupole transitions can be assigned to deuteriums bound to specific atoms, and to specific hydrogen bond locations within the structures of forms I and II.

Introduction

o-Aminobenzoic acid, commonly called anthranilic acid, is of considerable interest both in the biological sciences and in industrial processes.¹⁻³ In the solid state anthranilic acid exhibits polymorphism; three crystallographically distinct forms, differing only slightly in stability, can be

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