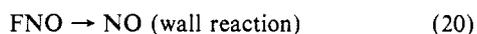
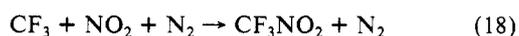
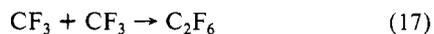


molecule⁻¹ s⁻¹ determined as *k* in this study. Typical fitting curves drawn in Figure 6 indicate excellent agreement, supporting this reaction mechanism quantitatively.

The formation of the final products, NO (major), C₂F₆, CF₃NO₂, and CF₄ (traces), and the slow decay of FNO can be explained by the following reaction:



The very low yield of CF₃NO₂ is consistent with the failure to observe the dependence of the decay of CF₃ on buffer gas pressure.

The pressure of FNO in the static cell increases with the laser irradiation, and therefore CF₄ may be produced by reaction 19. Most of FNO is presumably converted into NO via wall reactions.

Conclusion

In this paper, we have presented kinetics and mechanism for the reaction of CF₃ with NO₂. The time-resolved spectrum of CF₃ was observed by the diode laser spectroscopy. From the NO₂ pressure dependence of the decay rate of CF₃, the room temperature rate constant was determined to be $(2.5 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (3σ). Time-resolved spectra of FNO and CF₂O, appearing as the CF₃ decayed, were observed and interpreted in terms of the reaction path involving a four-centered transition state.

Registry No. CF₃, 2264-21-3; NO₂, 10102-44-0; CF₃I, 2314-97-8; FNO, 7789-25-5; CF₂O, 353-50-4; NO, 10102-43-9.

Second-Order Combination Reactions of Phenoxy Radicals¹

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Phenoxy radicals, when produced pulse radiolytically at concentrations >10⁻⁴ M, combine in second-order processes to give 2,2'-, 2,4'-, and 4,4'-dihydroxybiphenyl as the predominant products. The ratios of these products observed under a variety of conditions, 0.73:1.73:1.00, indicate that radical combination at the ortho and para positions of the ring occurs statistically with, however, reaction at the para site favored by a factor of 2.4 over that at the ortho site. This ratio is considerably greater than the ratio of 1.55 of the unpaired spin populations at the two sites as indicated by ESR data. There is essentially no reaction at the meta position where the unpaired spin population is negative. Approximately 10% of the radicals couple at oxygen to yield 2- and 4-phenoxyphenol. The yields of these two products are, however, considerably lower than might be expected from the unpaired spin population of 0.2 on the oxygen atom of phenoxy. It is clear that factors in addition to the unpaired spin population are important in controlling the combination processes. Under optimum conditions these five products account for ~90% of the phenoxy radicals initially produced so that electronic disproportionation or coupling to form diphenyl peroxide is relatively unimportant. Multiple-pulse experiments show that after products build up to concentrations comparable to that of the phenoxy radical, secondary electron-transfer reactions lead to more complex products. In studies with γ-rays at low-dose rates phenoxy radicals predominantly react with the products so that the yields of simple combination products are very low.

Introduction

ESR studies^{2,3} show that the unpaired spin population in phenoxy radical is highly delocalized with an appreciable fraction present on the 2- and 4-positions of the aromatic ring. It is of considerable interest to see how this delocalization is reflected in the reactions of these radicals. The qualitative observation that chemical oxidation of phenol leads to biphenyl hydroxylated at the 2- and 4-positions has been taken to indicate the involvement of a radical mechanism.⁴ Time-resolved optical,⁵ ESR,² and resonance Raman spectroscopic⁶ studies show that phenoxy radicals can be generated quantitatively under well-controlled conditions by radiation chemical methods. The Raman experiments⁶ show that in basic solutions at phenoxy concentrations of ~10⁻⁴ M the radicals predominantly decay in second-order processes having a rate constant (2*k*) of 2.6×10^9 M⁻¹ s⁻¹.⁶ A similar value (2.3×10^9 M⁻¹ s⁻¹) has been determined pulse

radiolytically in acidic solutions by absorption methods at radical concentrations more than 1 order of magnitude lower.⁷ In the present study we take advantage of pulse radiolytic approaches to explore quantitatively the effects of unpaired spin delocalization by examining the products of the second-order combination reactions of phenoxy radicals produced at relatively high concentrations. Because these radicals can be generated under well-controlled conditions in pulse radiolytic experiments, one can, to a large extent, avoid secondary processes that otherwise complicate interpretation of the observed product distribution in terms of site reactivity.

Experimental Section

Pulse irradiations were carried out with ~30-ns pulses of 2-MeV electrons from a Febetron 705 accelerator. Irradiations were 10–50 cm from the accelerator window at doses of (2–10) × 10¹⁸ eV/g per pulse. The Super-Fricke dosimeter (O₂-saturated 10 mM ferrous sulfate) was used for dosimetry. Irradiations were in a 2-cm-diameter flat cell 0.2–0.4 cm thick so that dose deposition was reasonably uniform within the cell volume. At the doses used, initial radical concentrations were 0.2–1 mM. A ⁶⁰Co γ-source, having a dose rate of 2.8×10^{16} eV g⁻¹ s⁻¹, was used for continuous irradiations. Solutions of 10⁻³–10⁻² M phenol at pH ~ 11 were purged of oxygen and saturated with N₂O to

(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-3081 from the Notre Dame Radiation Laboratory.

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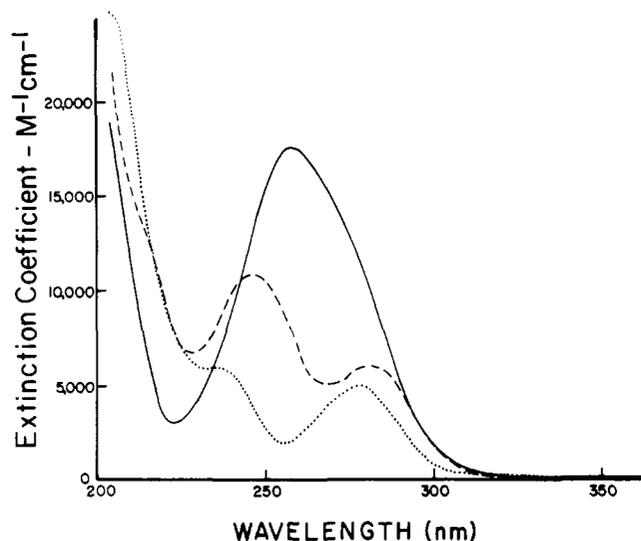


Figure 1. Absorption spectra of (—) 4,4'-dihydroxybiphenyl, (---) 2,4'-dihydroxybiphenyl, and (···) 2,2'-dihydroxybiphenyl. Spectra were recorded with a Hewlett-Packard 1040A diode array detector during the course of chromatographic analysis.

convert e_{aq}^- to $\cdot\text{OH}$. In most cases azide radical, prepared by $\cdot\text{OH}$ oxidation of 0.1 M sodium azide, was used as a secondary oxidant.⁸

Samples were analyzed by HPLC using an 8 mm \times 10 cm Waters NOVA-PAC C₁₈ radial compression column. Detection was with a Hewlett-Packard HP1040A diode array detector that permitted recording of spectra during the course of elution. Data were transferred to a VAX 11/780 computer for detailed analysis. Elution was with aqueous acetonitrile at pH \sim 3.5.

Solutions were made up from Aldrich Gold Label phenol with use of 18-M Ω water from a Millipore Milli-Q system. NaOH was used to adjust the pH. Sodium azide was from Fluka. Calibration samples were mostly from Aldrich. Samples of 2,4'-dihydroxybiphenyl and 2-phenoxyphenol were prepared by E. Rivera. Chromatographic analysis showed all reference materials to be >99% pure. Because the spectrum of 2,4'-dihydroxybiphenyl is not readily available, it is given in Figure 1 along with the spectra of the other two isomers of interest. It is noted that this spectrum exhibits two very distinct absorption bands at 250 and 285 nm. The longer wavelength band resembles the band at 280 nm in 2,2'-dihydroxybiphenyl. In 4,4'-dihydroxybiphenyl the shorter wavelength band is red-shifted to 265 nm so that the 280-nm band appears only as a shoulder on the long-wavelength side. In any event these three spectra are quite distinct and readily characterize the chromatographic components. Because of its shorter elution time and greater extinction coefficient the sensitivity for detecting 4,4'-dihydroxybiphenyl is considerably greater than for its isomers.

Results and Discussion

A previous study⁸ has shown that, in basic solutions in the presence of N₂O, phenoxide anion is rapidly and quantitatively oxidized to phenoxy by azide radical ($k_2 = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) with essentially no interference from other radicals present in the system. Azide radical prepared by $\cdot\text{OH}$ oxidation of 0.1 M sodium azide was used as a secondary oxidant in most of the present studies. Oxidation is by electron transfer to azide, which at 10^{-2} M phenoxide is essentially complete in 0.1 μs . With this approach all primary radicals including H atoms are converted to N₃ \cdot so that the radical system is totally oxidizing.⁵ This approach avoids the intermediary formation of cyclohexadienyl and hydroxycyclohexadienyl radicals that otherwise, as is shown below, interfere somewhat when one attempts to oxidize phenoxide directly by $\cdot\text{OH}$.

Typical chromatograms of a solution irradiated with a single pulse to a dose of 1.6×10^{18} eV/g (26000 rads) are given in Figure

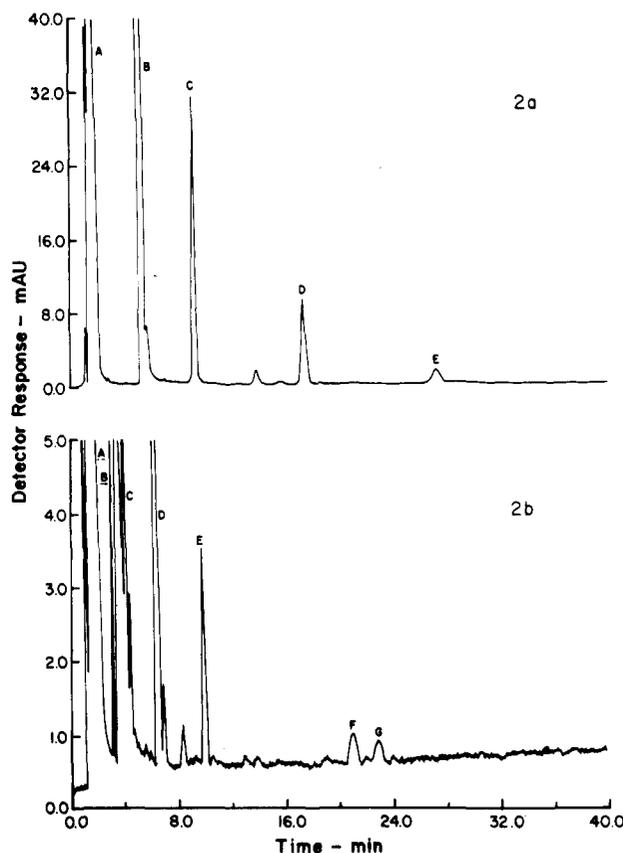
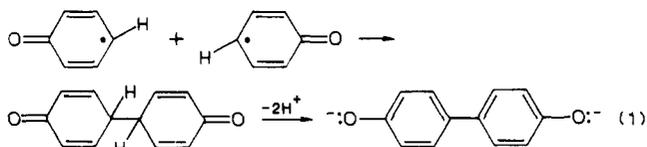


Figure 2. Chromatograms at 265 nm of a 10^{-2} M phenol solution at pH 11.3 (N₂O saturated) irradiated to a dose of 1.6×10^{18} eV/g with a single Febetron pulse. Elution in (a) was with 0.25:0.75 acetonitrile-water and in (b) was with 0.35:0.65 acetonitrile-water. Principal peaks are (A) azide, (B) phenol, (C) 4,4'-dihydroxybiphenyl, (D) 2,4'-dihydroxybiphenyl, (E) 2,2'-dihydroxybiphenyl, (F) 4-phenoxyphenol, and (G) 2-phenoxyphenol.

2. At this dose the initial radical concentration is 1.6×10^{-4} M. Raman experiments⁶ show that at this concentration phenoxy radicals have a median lifetime toward second-order decay of 2.4 μs . Side reactions interfere significantly with radical combination only if their pseudo-first-order rate constants are greater than $\sim 10^5 \text{ s}^{-1}$; i.e., reaction with impurities or products can be important only at concentrations greater than 10^{-4} M. The five major product peaks in Figure 2 are identified from their elution times and characteristic absorption spectra as (C) 4,4'-dihydroxybiphenyl, (D) 2,4'-dihydroxybiphenyl, (E) 2,2'-dihydroxybiphenyl, (F) 4-phenoxyphenol, and (G) 2-phenoxyphenol. Very weak contributions from a number of unidentified products are apparent in Figure 2, but only the peak eluted at 14 min in Figure 2a is observed with any significant intensity. These five products result from radical combination at the positions of appreciable unpaired spin population, i.e., at oxygen and at the 2- and 4-positions of the ring. There is no evidence for any significant yield of diphenyl peroxide that would be attributable to coupling at the oxygen positions. It is possible that this product either is destroyed in the radiolysis or does not survive the analysis. We note that the initial combination products must lose two protons to form the observed products. For example, coupling of unpaired spins at the para positions results in a radical that subsequently deprotonates to 4,4'-dihydroxybiphenyl.



Deprotonation appears to be strongly catalyzed by azide ion (see ref 9) so that the overall reaction is somewhat simpler when high

TABLE I: Product Yields in Pulse Irradiation of Aqueous Solutions of Phenol^a

abs dose, eV/g $\times 10^{-18}$	dihydroxybiphenyls			phenoxy-phenols	
	4,4'	2,4'	2,2'	4	2
1.6	0.66	1.13	0.49		
1.6	0.66	1.14	0.47	0.23	0.10
1.9	0.67	1.14	0.52		
1.9	0.67	1.15	0.48	0.22	0.10
2.6	0.66	1.14	0.41		
4.0	0.66	1.16	0.47		
6.3	0.66	1.16	0.56		
10.0	0.64	1.14	0.45		
abs yield (G) ^b	0.66	1.15	0.48	0.23	0.10
rel yield	1.00	1.74	0.73	0.35	0.15

^aDose delivered in ~ 30 ns by Febetron 705 accelerator. Yields are given in units of *G* (molecules/100 eV). Averages of four experiments. All solutions saturated with N_2O . ^bThe total yield of the five products is 2.62.

concentrations of azide are present.

Time-resolved Raman experiments⁶ show definitively that as the products of radical combination build, they are oxidized further by the remaining phenoxyl radicals. Electron transfer from 4,4'-dihydroxybiphenyl to phenoxyl, for example, has a rate constant $\sim 2 \times 10^9 M^{-1} s^{-1}$.¹⁰ Since the rate constants for these electron-transfer processes are only slightly lower than for radical combination, small yields of more complicated products are necessarily unavoidable. Complications can become quite important during the final stages of radical decay and depend to a considerable extent on how rapidly deprotonation occurs. The Raman experiments show that, in the presence of 0.1 M azide, side reactions result in a lower concentration of phenoxyl on the microsecond time scale only during the last $\sim 10\%$ of radical decay. The chromatographic studies also show that side reactions are at a minimum when azide is used as the oxidant.

The yields of the five major products measured at different doses in single-pulse experiments are given in Table I. It is seen that the yields of 4,4'- and 2,4'-dihydroxybiphenyl are quite constant and not dependent on dose. The values for 2,2'-dihydroxybiphenyl scatter somewhat because of the relatively low sensitivity for this component, but there appears to be no significant trend with dose. In summary, at initial radical concentrations in the range 0.16–1.0 mM these five products (C–G in Figure 2, respectively) are produced in the ratio 1:1.74:0.73:0.35:0.15. The yield of azide radicals available for oxidizing phenoxide is currently somewhat in question because of loss of azide radicals in spur processes and because of delays in their production by reaction of H atoms with azide.⁵ However, a yield of 5.8, based on the sum of the yields of OH radicals that escape from the spurs and H atoms, is reasonable. The total yield of 2.62 in Table I represents a phenoxyl yield of 5.2 or $\sim 90\%$ of the phenoxyl radicals initially produced.

Because of the importance of the reaction of phenoxyl radicals with the products it is interesting to examine the consequences of delivering the dose in a number of sequential pulses. Figure 3 gives chromatograms of a sample exposed to five pulses similar to those used in Figure 2. These pulses were delivered at ~ 5 -min intervals. Comparison of Figures 2 and 3 shows that the yields of the combination products are only about twice those of samples given a single pulse and that there is a considerably greater yield of side products, particularly in the region where the phenoxy-phenols elute. The yields of the dihydroxybiphenyls observed in experiments of this type are summarized in Table II. The total amount of dihydroxybiphenyl produced approaches a limit of the order of twice that from a single pulse so that pulses late in the sequence produce very little additional net amounts of these products. It is clear from the data of this table that the products

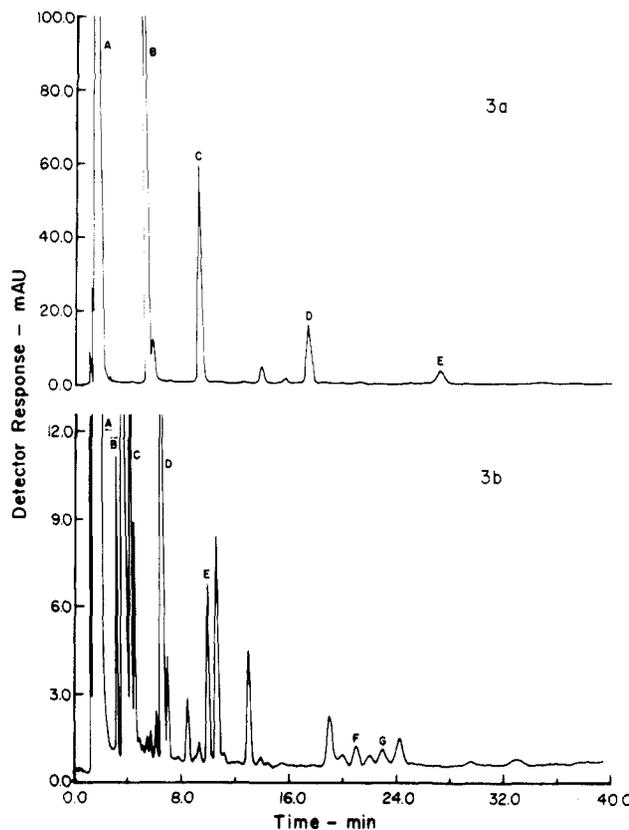


Figure 3. Chromatograms similar to those of Figure 2 but for samples irradiated to a dose of 8×10^{18} eV/g in five pulses spaced at ~ 5 -min intervals.

are rapidly consumed by tertiary electron-transfer reactions. It is seen in Table II that the relative yield of 2,4'-dihydroxybiphenyl decreases somewhat more rapidly than does that of the other isomers. It appears to be more susceptible to tertiary reactions. However, the effect is small and the ratios are approximately as for a single pulse even in the case of ten pulses, where 80% of the phenoxyl radicals are lost to reaction with the products.

Experiments with continuous ^{60}Co irradiation at a dose rate of 2×10^{18} eV $g^{-1} min^{-1}$ show even more dramatic effects of these tertiary processes. As illustrated by the chromatogram in Figure 4a, one does not observe any significant yield of the simple combination products at a total dose comparable to that in the pulse experiment of Figure 2. At a 10-fold greater dose (Figure 4b) small yields of a number of other products, but essentially no radical combination products, are observed. Combination products must be formed, but they apparently are of high molecular weight and not readily eluted from the column. At the dose rate of this experiment the phenoxyl production rate is $\sim 3 \times 10^{-6}$ M/s so that its concentration does exceed 3×10^{-8} M during the irradiation. At such a low concentration (less than 1% of the products) phenoxyl radicals react with products long before they encounter a second phenoxyl radical. Radical combination reactions must ultimately occur, but they apparently involve relatively high molecular weight radicals formed in a chain of electron-transfer processes.

The production of the dihydroxybiphenyls was examined under other conditions of phenoxyl preparation, and the results are summarized in Table III. In experiments with 1 mM phenol at pH 11.4, where the period for oxidation of phenoxide by N_3^* is $\sim 0.2 \mu s$, the yields are about 50% lower. We note, however, that the product yields are in approximately the same ratio as in Table I. In these cases about 20% of the phenol is oxidized so that it is not surprising that an appreciable fraction of the products is lost in tertiary processes. In addition, because the rate constant for the combination of azide radicals is very high ($k \sim 10^{10} M^{-1} s^{-1}$),⁸ a fraction (10–20%) of the oxidant will be lost because of the relatively longer oxidation period. One clearly needs to carry out the experiment at substrate concentrations $> 10^{-2}$ M to ensure

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TABLE II: Effect of Multipulse Irradiation on Product Yields^a

no. of pulses	total dose, eV/g $\times 10^{-18}$	dihydroxybiphenyls ^b			phenoxyphenols		total
		4,4'	2,4'	2,2'	4	2	
1	1.6	0.66	1.14	0.48	0.23	0.10	2.60
2	3.2	0.37	0.53	0.31	0.10	0.06	1.36
5	8.0	0.33	0.44	0.25	0.07	0.04	1.13
10	16.0	0.16	0.20	0.14	0.04	0.03	0.57

^aDose delivered in similar pulses spaced by ~ 5 min. Yields are given in units of G (molecules/100 eV). ^bRelative yields of 4,4'-dihydroxybiphenyl, 2,4'-dihydroxybiphenyl, and 2,2'-dihydroxybiphenyl: for two pulses, 1:1.43:0.84; for five pulses, 1:1.33:0.75; for ten pulses, 1:1.25:0.88.

TABLE III: Production of Dihydroxybiphenyls under Varying Conditions^a

soln	abs dose, eV/g $\times 10^{-18}$	dihydroxybiphenyl				product ratio: 4,4':2,4':2,2'
		4,4'	2,4'	2,2'	total	
1 mM phenol, 0.1 M NaN ₃ , pH ~ 11.4	2.0	0.38	0.64	0.21	1.22	1.0:1.68:0.55
	1.87	0.34	0.56	0.24	1.15	1.0:1.64:0.71
	2.30	0.35	0.58	0.26	1.19	1.0:1.65:0.73
10 mM phenol, ^b pH ~ 11.3	1.87	0.51	0.86	0.39	1.76	1.0:1.69:0.77
	1.31	0.56	0.89	0.26	1.71	1.0:1.59:0.46
10 mM phenol, 0.1 M NaN ₃ , pH ~ 7.3	1.64	0.38	0.66	0.28	1.32	1.0:1.74:0.74
10 mM phenol, ^b pH ~ 7.4	1.64	0.13	0.23	0.12	0.48	1.0:1.77:0.92

^aAll solutions saturated with N₂O. ^bDirect oxidation by $\cdot\text{OH}$.

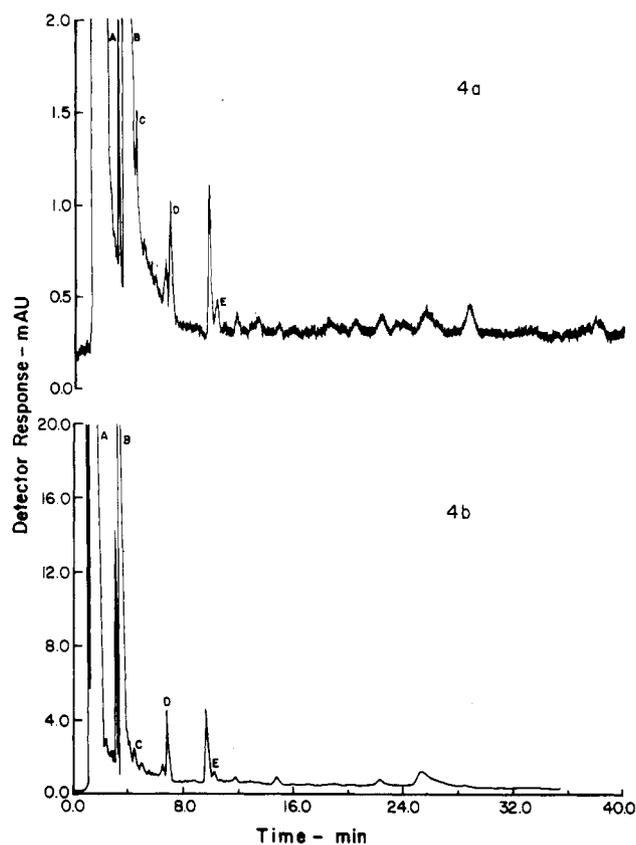


Figure 4. Chromatograms of a 10^{-2} M phenol solution at pH 11.3 (N₂O saturated) irradiated with ⁶⁰Co γ -rays at a dose rate of 2.8×10^{16} eV g⁻¹ s⁻¹ to doses of (a) 1.7×10^{18} eV/g and (b) 1.7×10^{19} eV/g. Elution was as in Figure 2b.

more nearly quantitative conversion of azide radical to phenoxy. In these experiments at 10^{-2} M phenoxide a small fraction ($\sim 5\%$) of the azide radicals is lost to second-order reactions between azide radicals.

In the experiments at pH ~ 7 with azide radical as the oxidant noted in Table III, one finds that the yields are similarly low even though the solutions are 10 mM phenol. At this pH, phenol is present in its protonated form and oxidation by azide radical is relatively slow ($k = 2 \times 10^8$ M⁻¹ s⁻¹).⁸ The decrease appears to be almost entirely attributable to loss of azide radicals before they can react with the substrate. It is noted that in spite of the lower

yield the product ratios are as in Table I.

Hydroxyl radicals oxidize phenol and phenoxy mainly by addition followed by the loss of OH⁻ rather than by electron transfer.¹¹ When OH radical was used directly as the oxidant in basic solutions, the yields (see Table III) were $\sim 20\%$ lower than when azide was used. Complications are apparent but appear to have been relatively minor. These complications very likely relate more closely to the deprotonation of the combination product than to the phenoxy-formation process. When similar studies are carried out in neutral (or acidic) solutions the yields of dihydroxybiphenyls are only $\sim 20\%$ of those found when azide radical is used as the oxidant. In these latter experiments, the OH adducts (hydroxylated hydroxycyclohexadienyl radicals) are relatively stable⁹ and the phenoxy radicals are produced relatively slowly. Their concentration never becomes very high and, as in the γ -radiolysis experiments, side reactions dominate their fate.

In spite of the various complications manifested in Table III it is noted that the ratios of the three principal products are about as in Table I. The product ratios of 1:1.74:0.73 indicated in the discussion of the data of Table I are very nearly the coefficients of the expansion of $(a + 0.86b)^2$, indicating that reaction at the ortho and para positions occurs statistically. Taking into account the 2-fold greater number of ortho sites, the probability for reaction at an ortho position is only 43% that at the para position. This ratio is considerably lower than the ratio of 0.65 expected from the unpaired spin populations of 0.26 and 0.41 at the ortho and para positions as indicated by the respective proton hyperfine constants of 6.61 and 10.22 G.³ The ortho site is, therefore, only 66% as reactive as one might expect from the relative unpaired spin populations. Many factors including both steric and electronic contributions can, of course, play a role in discriminating in favor of reaction at the para position.

The unpaired spin population at each of the meta positions is -0.07 so it is not surprising that no significant reaction is observed at this position. By difference, the unpaired spin directly on the oxygen is estimated to be 0.21. Coupling at the oxygen to form the phenoxyphenols is surprisingly poor in view of this appreciable population. The yield of 4-phenoxyphenol is only one-third that of 4,4'-dihydroxybiphenyl, whereas it should be greater by a factor of 1.02 (i.e., $2 \times 0.21/0.41$) if the reaction frequencies corresponded to the relative unpaired spin populations. Steric problems should not play a direct role in this case as they might in the case of reaction at the ortho position. The relative yield of 2-phenoxyphenol is very much lower, only about one-tenth that expected from the spin populations and one-fifth that from the reactivities

noted above in coupling at the ring positions. In general the product distributions make it clear that factors other than the spin populations play an important role in directing the spin pairing involved in radical combination.

We note that electron transfer from one phenoxy radical to another, which would yield hydroquinone as the oxidized product, does not appear to be of major importance in the second-order reactions between phenoxy radicals. Apparently the oxidation and reduction potentials of phenoxy radicals are not sufficiently matched to permit ready transfer of an electron from one radical to another.

In conclusion we remark that the studies reported here illustrate

very well the application of radiation chemical methodology to a problem that would be difficult to resolve by more conventional techniques. The simplicity of using ionizing radiation to initiate a chemical process under well-controlled conditions has made this study possible.

Acknowledgment. We thank Edwin Rivera for providing the samples of 2,4'-dihydroxybiphenyl and 2-phenoxyphenol used as references in these studies. The assistance of Ralph Steinback in the operation of the Febetron is acknowledged.

Registry No. Phenoxy, 2122-46-5; 4,4'-dihydroxybiphenyl, 92-88-6; 2,4'-dihydroxybiphenyl, 611-62-1; 2,2'-dihydroxybiphenyl, 1806-29-7.

Oxidation of Phosphorus(III) Halides by Red Photolysis of Ozone Complexes in Solid Argon

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$\text{PCl}_3\text{-O}_3$ and $\text{PBr}_3\text{-O}_3$ complexes in solid argon photolyze to give phosphoryl halides with red visible radiation that has no effect on isolated ozone. These observations and similar results for $\text{PH}_3\text{-O}_3$ and $\text{P}_4\text{-O}_3$ complexes show that the complex markedly increases the cross section for red photodissociation of ozone and suggest that this increase is due to the complex effectively lowering the barrier to dissociation by providing a strongly exothermic dissociation-recombination process.

Introduction

Recent infrared spectroscopic work in our laboratories has shown that molecular complexes are formed between phosphine and ozone and between arsine and ozone in low-temperature argon matrices^{1,2} and that when these complexes are irradiated with red visible wavelengths, the ozone submolecule is photolyzed. Reaction of the photolytically liberated oxygen atoms with the phosphine submolecule produced several previously unreported primary and secondary products.³ We have extended this work by examining the photolysis of ozone in matrices containing the phosphorus(III) halides PF_3 , PCl_3 , and PBr_3 to generate simple compounds of phosphorus, halogen, and oxygen and also to explore the dependence of the nature and magnitude of product yield on photolysis wavelength.

Experimental Section

Apparatus. The low-temperature cell consisted of a cylindrical stainless steel vacuum chamber fitted with the cold head of a closed-cycle helium refrigerator (CTI-Cryogenics, Model 22). Attached to the cold head was a OFHC copper block containing a cesium iodide window affixed with indium gaskets. The cell mounting was surrounded by an aluminum radiation shield with ports oriented to allow access to the tips of spray-on lines and to allow a light path for spectroscopic study of sample deposit. Sample temperatures were measured by a diode attached to the cold head and connected to a temperature controller (Lake Shore Cryotronics Model DRC 80C), which also provided power to a heater used in warming samples.

Samples were made up in, and deposited from, two different stainless steel spray-on lines, their openings pointing perpendicular to the axis of the vacuum chamber and toward the center of the CsI window.

Spectra were taken with a grating infrared spectrophotometer (Perkin-Elmer Model 983) connected to a data station (Perkin-Elmer Model 3600). Survey spectra were recorded from 4000

to 180 cm^{-1} with a resolution of 3 cm^{-1} . High-resolution spectra were taken of spectral regions within this range with a resolution of 1 cm^{-1} . Wavenumber accuracy is $\pm 0.5\text{ cm}^{-1}$. Visible-ultraviolet spectra were recorded on a grating spectrophotometer (Cary 17).

Photolyses were carried out by using a 1-kW high-pressure mercury arc lamp (BH-6, Illumination Ind., Inc.) in combination with a 10-cm water filter and Corning glass filters. Irradiation wavelengths employed by using these filters were 360-470, 340-600, 630-1000, 520-1000, 420-1000 nm, and full mercury arc (220-1000 nm).

Materials. Phosphorus(III) bromide and phosphorus(III) chloride (Aldrich) were used as received and were degassed by several freeze-pump-thaw cycles on the vacuum manifold. Phosphorus(III) fluoride (PCR Research Chemicals) was used without further purification. Ozone ($^{16}\text{O}_3$) was generated by tesla coil discharge of $^{16}\text{O}_2$ (Matheson) in a Pyrex tube immersed in liquid nitrogen;⁴ residual dioxygen was removed by pumping with a rotary pump. Ozone containing a mixture of isotopes was generated by tesla coil discharge of a sample of O_2 enriched to 55% ^{18}O (Yeda Stable Isotopes), and $^{18}\text{O}_3$ was generated from O_2 enriched to 98% ^{18}O (Yeda). Argon (Air Products) was used as received.

Methods. Samples of Ar/PCl_3 (150/1) and Ar/PF_3 (200/1) were prepared by admitting measured aliquots of phosphorus(III) halide into the vacuum manifold and then diluting with argon in a 3-L stainless steel can attached to the manifold. Samples of Ar/PBr_3 were prepared by allowing PBr_3 to reach its saturation vapor pressure in the manifold-can system and then diluting the vapor with argon; concentrations were estimated by using the literature value for PBr_3 vapor pressure. Samples of Ar/O_3 (150/1 or 200/1) were prepared by allowing liquid ozone, prepared by

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