A Kinetic and Mechanistic Study of the Self-Reaction and Reaction with HO₂ of the Benzylperoxy Radical

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The kinetics and mechanism of the reactions $C_6H_5CH_2O_2 + C_6H_5CH_2O_2 \rightarrow 2C_6H_5CH_2O + O_2$ (3a), $C_6H_5-CH_2O_2 \rightarrow 2C_6H_5CH_2O + O_2$ (3a), $C_6H_5-CH_2O_2 \rightarrow 2C_6H_5CH_2O + O_2$ $CH_2O_2 + C_6H_5CH_2O_2 \rightarrow C_6H_5CHO + C_6H_5CH_2OH + O_2$ (3b), and $C_6H_5CH_2O_2 + HO_2 \rightarrow C_6H_5CH_2OOH$ $+ O_2$ (4) have been investigated using two complementary techniques: flash photolysis/UV absorption for kinetic measurements and continuous photolysis/FTIR spectroscopy for end-product analyses and branching ratio determinations. The reaction of chlorine atoms with toluene was found to yield benzyl radicals exclusively and was used to generate benzylperoxy radicals in excess oxygen. During this study, relative reaction rate constants of chlorine atoms with compounds related to those involved in the reaction mechanism have been measured at room temperature: $k(Cl+toluene) = (6.1 \pm 0.2) \times 10^{-11}$, $k(Cl+benzaldehyde) = (9.6 \pm 0.4) \times 10^{-11}$ 10^{-11} , $k(Cl+benzyl chloride) = (9.7 \pm 0.6) \times 10^{-12}$, $k(Cl+benzyl alcohol) = (9.3 \pm 0.5) \times 10^{-11}$, k(Cl+benzene) $< 5 \times 10^{-16}$, all in units of cm³ molecule⁻¹ s⁻¹. The products identified following the self-reaction 3 were benzaldehyde, benzyl alcohol, and benzyl hydroperoxide. The latter is the product of the reaction of C_6H_5 -CH₂O₂ with HO₂. The yield of products allowed us to determine the branching ratio $\alpha = k_{3a}/k_3 = 0.4$. The UV absorption spectrum of the benzylperoxy radical was determined from 220 to 300 nm. It was similar to those of alkylperoxy radicals, with a maximum cross section at 245 nm of 6.8×10^{-18} cm² molecule.⁻¹ Kinetic data were obtained from the detailed simulation of experimental decay traces recorded at 250 nm over the temperature range 273-450 K. The resulting rate expressions are $k_3 = (2.75 \pm 0.15) \times 10^{-14} \exp[(1680 \pm$ 140 K/T] cm³ molecule⁻¹ s⁻¹ and $k_4 = (3.75 \pm 0.32) \times 10^{-13} \exp[(980 \pm 230)$ K/T) cm³ molecule⁻¹ s⁻¹ (errors = 1σ). The UV absorption traces in the flash-photolysis kinetic study were well accounted for by the identified products in the FTIR study, thus providing good confidence in the results. However, about 20% of the products have remained unidentified. Some uncertainties persist in the reaction mechanism leading us to assign a fairly large uncertainty of about 50% to the rate constants k_3 and k_4 over the whole temperature range. This work shows that the aromatic substituent does not provide any specificity in the reactivity of peroxy radicals and confirms that large radicals tend to react faster with HO₂ than generally assumed in current atmospheric models.

Introduction

The kinetics and mechanism of peroxy radicals, "RO₂", have received a good deal of attention in recent years. The available literature has been reviewed recently.^{1,2} However, although a substantial database now exists for alkylperoxy and some of the simplest substituted alkylperoxy radicals, very little is known about the gas-phase chemistry of peroxy radicals derived from aromatic compounds. Tropospheric sources of aromatic compounds include motor vehicle exhausts, paints, solvents, and vegetation.³ Of the aromatic hydrocarbons, toluene has the highest typical ambient concentration in urban areas.⁴ Toluene is degraded in the troposphere via reaction with OH radicals, and around 10% of the overall reaction of OH with toluene is thought to proceed via hydrogen abstraction from the methyl group⁴

$$C_6H_5CH_3 + OH \Leftrightarrow adduct$$
 (1a, -1a)

$$H_{2}O + C_{6}H_{5}CH_{2}$$
 (1b)

leading, in the presence of excess oxygen, to the formation of

benzylperoxy radicals, C₆H₅CH₂O₂:

$$C_6H_5CH_2 + O_2 + M \rightarrow C_6H_5CH_2O_2 + M \qquad (2)$$

Of the reactions of the benzylperoxy radical likely to be important in the atmosphere, only the ratio of the rate constants of the reactions with NO and NO₂ has been measured.^{5,6} No other kinetic or mechanistic information is available. The present study was undertaken to provide further information on the reactivity of the benzylperoxy radical and, more generally, on peroxy radicals bearing an aromatic substituent.

This paper presents the results of a kinetic and mechanistic study of the self-reaction of the benzylperoxy radical:

$$C_6H_5CH_2O_2 + C_6H_5CH_2O_2 \rightarrow \text{products}$$
 (3)

and of its reaction with the hydroperoxy radical:

$$C_6H_5CH_2O_2 + HO_2 \rightarrow products$$
 (4)

The reported data were obtained in a collaborative study of reactions 3 and 4, in which complementary techniques were used. In Dearborn, end-product analysis using FTIR spectroscopy was

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used to determine the products and branching ratios of the reactions, while in Bordeaux, flash photolysis with UV absorption detection of radicals was used for the determination of the reaction kinetics and of the UV absorption spectrum of the benzylperoxy radical.

The benzylperoxy radical was generated in both studies by photolyzing molecular chlorine in the presence of toluene:

$$Cl_2 + h\nu \rightarrow 2Cl$$
 (5)

$$Cl + C_6H_5CH_3 \rightarrow HCl + C_6H_5CH_2$$
(6)

 k_6 /cm³ molecule⁻¹ s⁻¹ = 6.1 × 10⁻¹¹

(determined in this work)

$$C_6H_5CH_2 + O_2 + M \rightarrow C_6H_5CH_2O_2 + M$$
 (2)

 k_2 /cm³ molecule⁻¹ s⁻¹ = 1.05 × 10⁻¹²,

independent of pressure⁷

To provide added insight into reaction 6 and to assess the possible importance of secondary reactions in the present system, relative rate studies were performed to determine the rate constants for the reactions of Cl atoms with toluene, benzene, benzyl chloride, benzyl alcohol, and benzaldehyde.

FTIR Study

Experiment. The apparatus and experimental techniques used have been described in detail previously⁸ and are only briefly discussed here. All experiments were performed in a 140-L Pyrex reactor surrounded by 22 fluorescent blacklamps (GE F15T8-BL) which were used to initiate our experiments, by photolysis of molecular chlorine.

The loss of toluene and the formation of products were monitored by Fourier transform infrared spectroscopy using an infrared path length of 26.6 m and a resolution of 0.25 cm⁻¹. Infrared spectra were derived from 32-128 co-added interferograms. Reference spectra were obtained by expanding known volumes of the reference material into the long-path length cell. Products were identified and quantified by fitting reference spectra of the pure compounds to the observed product spectra using integrated absorption features over the following wavelength ranges (in cm⁻¹): toluene, 1000-1100; benzaldehyde, 775-850 and 1700-1750; benzyl chloride, 650-850 and 1200-1300; benzyl dichloride, 700-1400; benzyl alcohol, 650-1450 and 3640-3680. A reference spectrum for the hydroperoxide C₆H₅CH₂OOH was unavailable; yields of this product were estimated by comparing the integrated absorption over the region 3560-3610 cm⁻¹ with that of a calibrated spectrum of C₂H₅OOH acquired earlier.⁸ To check this approach, the absorption features in the region 3575-3625 cm⁻¹ in our calibrated reference spectra of CH₃OOH, C₂H₅-OOH, and $t-C_4H_9OOH$ were compared. The integrated absorptions agreed to better than 10%.

Calibration of the reference spectrum of benzyl alcohol was indirect. Benzyl alcohol has a low vapor pressure (<0.1 Torr at 295 K). To introduce a measurable amount of benzyl alcohol into the chamber, part of the flow of synthetic air used to fill the chamber was passed over the alcohol sample. To calibrate the resulting spectrum, Cl₂ was added and the mixture irradiated. Reaction of Cl atoms with benzyl alcohol is expected to produce benzaldehyde and HCl both in 100% yield by the following reactions: The Journal of Physical Chemistry, Vol. 98, No. 11, 1994 2865

$$C_6H_5CH_2OH + Cl \rightarrow C_6H_5CHOH + HCl \qquad (7)$$

$$C_6H_5CHOH + O_2 \rightarrow HO_2 + C_6H_5CHO$$
 (8)

The yields of benzaldehyde and HCl were indistinguishable (within 10%), suggesting that one benzaldehyde is produced for every benzyl alcohol consumed in accordance with reaction 7 and 8 and that HO₂ radicals do not react with benzaldehyde in the chamber. The benzyl alcohol spectrum was then calibrated relative to the average of the HCl and benzaldehyde yield.

In a limited subset of the present experiments, a triple quadrupole mass spectrometer (Sciex, API-III) was available as an additional analytical tool for the measurement of benzaldehyde. Reaction mixture samples were withdrawn from the chamber via a 3-mm \times 2-m unheated Teflon line into the Sciex API-III triple quadrupole mass spectrometer.

Nitric oxide chemical ionization was used to produce the M-H+ ion $(m/z \ 105)$ of benzaldehyde. Nitric oxide is generated in a low-pressure glow discharge ion source from nitrogen and oxygen in ultrapure air. The nitric oxide, in a well-known reaction,⁹ extracts the hydrogen on the aldehyde functionality in the form of a hydride (H⁻), forming the positive M-H⁺ ion. This ion (m/z)105) was selected by the first quadrupole for collisional fragmentation in the second quadrupole, and the m/z 77 fragment ion (benzaldehyde-CHO)+ was detected selectively, by the third quadrupole. This chemical ionization and collision-induced fragmentation pathway was confirmed using a gas standard of benzaldehyde. Typical sensitivities were 320 000 ion counts s⁻¹ ppm⁻¹ benzaldehyde introduced into the ion source. The instrument response was linear from 1 ppb to 1 ppm. During analysis, the sample from the smog chamber was diluted by a constant factor so that measurement of the benzaldehyde in the smog chamber fell within this linear range. No interferences by the precursors or known reaction products were observed.

Initial concentrations of the gas mixtures for the relative rate experiments were 5–25 mTorr of the reactant and reference organics with 100 mTorr of Cl_2 in the presence of 700 Torr of either N_2 or air diluent. In the study of the self-reaction of benzylperoxy radicals the initial concentrations were 100–450 mTorr of toluene, 100–400 mTorr of Cl_2 , and 15–700 Torr of O_2 , with N_2 added as appropriate to maintain a total pressure of 700 Torr. All experiments were performed at 295 K. N_2 and O_2 were zero grade with stated purities of 99.998% and 99.6%, respectively. All other reagents were purchased from commercial vendors at purities of >99% and were used without further purification.

With the exception of our determination of benzyl alcohol and the hydroperoxide $C_6H_5CH_2OOH$, we estimate that potential systematic uncertainties associated with our quantitative analyses are <10%. For benzyl alcohol and $C_6H_5CH_2OOH$ we estimate that possible systematic errors are <20%.

Results. FTIR Study of the Reaction of Cl Atoms with Toluene. Prior to our kinetic and mechanistic study of the selfreaction of benzylperoxy radicals, it is critical to establish the yield of benzyl radicals following reaction of Cl atoms with toluene. To provide such information, experiments were performed in the absence of oxygen, in which mixtures of 100–130 mTorr of toluene and 100–415 mTorr of chlorine were irradiated in 700 Torr of nitrogen diluent. Three products were observed following such irradiations: benzyl chloride, benzyl dichloride, and benzaldehyde. After subtraction of IR features attributable to these three products no residual IR features remained.

The observed yields of benzyl chloride and benzaldehyde are plotted versus the loss of toluene in Figure 1. As seen from this figure, the yields of benzyl chloride and benzaldehyde were independent of the consumption of the toluene (4-20%). In contrast, the benzyl dichloride product yield increased from a trace amount (approximately 1% yield) at low conversions of



Figure 1. Plot of the observed yields of benzyl chloride and benzaldehyde versus the loss of toluene following irradiation of toluene/ Cl_2/N_2 mixtures at 700 Torr total pressure and 295 K.

toluene to approximately 4% at the highest conversion. Linear least-squares analysis of the data in Figure 1 gives molar products yields of $86 \pm 8\%$ for benzyl chloride and $4 \pm 1\%$ for benzaldehyde. Quoted errors are 2 standard deviations. Benzyl chloride is formed by the reaction of benzyl radicals with molecular chlorine, subsequent chlorination leads to the dichloride:

$$C_6H_5CH_3 + Cl \rightarrow C_6H_5CH_2 + HCl$$
(6)

$$C_6H_5CH_2 + Cl_2 \rightarrow C_6H_5CH_2Cl + Cl$$
(9)

$$C_6H_5CH_2Cl + Cl \rightarrow C_6H_5CHCl + HCl$$
 (10)

$$C_6H_5CHCl + Cl_2 \rightarrow C_6H_5CHCl_2 + Cl \qquad (11)$$

The benzaldehyde product we observe presumably arises from reaction of benzyl radicals with traces of molecular oxygen impurity in our N₂ diluent. Using $k_9/k_2 = 1.2$,⁷ we calculate that the O₂ impurity was approximately 6% of the Cl₂ concentration, i.e., 6–24 mTorr. In 700 Torr of N₂ this represents a 0.0009–0.003% impurity, which does not seem unreasonable. All three products we observe are consequences of Cl atom attack of the methyl group in toluene. Within our experimental uncertainties, the products benzyl chloride, benzyl dichloride, and benzaldehyde together account for all of the observed loss of toluene. No other carbon-containing products were observed.

To provide added insight into the reaction of Cl atoms with toluene and to assess the possible importance of secondary reactions in the present system, relative rate studies were performed to determine the rate constants for the reactions of Cl atoms with toluene, benzene, benzyl chloride, benzyl alcohol, and benzaldehyde. The experimental techniques employed in such studies have been described previously.8 Several reference compounds were used as appropriate: ethene, ethane, ethyl chloride, methane, and methane- d_4 . Experiments were performed at 700 Torr total pressure. Experiments for each reactant/ reference pair were performed in both N_2 and air diluent. With the exception of experiments using benzene, results obtained in both diluents were indistinguishable. Representative results obtained using toluene as reactant and ethene as reference are shown in Figure 2. Linear least-squares analysis of the data shown in Figure 2 and analogous plots give the rate constant ratios listed in Table 1.

The rate constant ratios given in Table 1 can be placed on an absolute basis using literature values for the reference rate constants: $k(Cl+C_2H_4) = 9.3 \times 10^{-11}$, $k(Cl+C_2H_6) = 5.7 \times 10^{-11$



Figure 2. Observed loss of toluene versus ethene loss following UV irradiation of toluene/ethene/ Cl_2 mixtures in 700 Torr of air (O) or nitrogen diluent (\bullet) at 295 K.

TABLE 1: Measured Rate Constant Ratios^a

	reference				
reactant	C ₂ H ₄	C ₂ H ₆	C ₂ H ₅ Cl	CH4	CD4
toluene	0.66 ± 0.02				-
benzaldehyde	1.01 ± 0.04	1.69 ± 0.07			
benzene				<0.07 ^b	<0.07
benzyl chloride		0.17 ± 0.01	1.00 ± 0.04		
benzyl alcohol	1.00 ± 0.05				

^a Quoted errors are 2 standard deviations. ^b Nitrogen diluent.

 10^{-11} ,¹¹ $k(Cl+C_2H_5Cl) = 8.0 \times 10^{-12}$,¹² $k(Cl+CH_4) = 1.0 \times 10^{-13}$,¹¹ and $k(Cl+CD_4) = 6.1 \times 10^{-15}$.¹³ Hence, we derive $k_6 = (6.1 \pm 0.2) \times 10^{-11}$, $k_{12} < 5 \times 10^{-16}$, $k_{13} = (9.6 \pm 0.4) \times 10^{-11}$, $k_{10} = (9.7 \pm 0.6) \times 10^{-12}$, and $k_{14} = (9.3 \pm 0.5) \times 10^{-11}$ (all in units of cm³ molecule⁻¹ s⁻¹).

$$Cl + C_6 H_6 \rightarrow products$$
 (12)

$$Cl + C_6H_5CHO \rightarrow products$$
 (13)

$$Cl + C_6H_5CH_2Cl \rightarrow products$$
 (10)

$$Cl + C_6H_5CH_2OH \rightarrow products$$
 (14)

The reactivities of benzaldehyde and benzyl chloride were measured relative to two different reference compounds. When placed upon an absolute basis, the results obtained relative to the two different reference compounds are indistinguishable. Ethane was used as a reference for the studies involving both benzaldehyde and benzyl chloride and was chosen as our standard in the derivation of our values for k_{10} and k_{13} .

As noted above, for experiments involving benzene a significant difference in results was observed with the two different diluents used. With air diluent, plots of the decay of benzene versus that of methane were curved, with a decreasing benzene loss observed at longer irradiation times. With nitrogen diluent there was no observable benzene loss, while methane was all consumed. We ascribe this behavior to complications associated with the production of OH radicals in the chamber. Modeling calculations have shown previously¹⁴ that OH radicals can be formed in Cl atom competitive kinetics studies of low-reactivity reactants in the presence of oxygen, leading to curvature in relative rate plots.¹⁴ The mechanism by which OH radicals are formed is thought to involve reaction of Cl atoms with hydroperoxides. The Cl atominitiated oxidation of methane produces a significant yield of methyl hydroperoxide,^{1,2} which can react with Cl atoms to give OH radicals.

$$CH_3OOH + Cl \rightarrow CH_2OOH + HCl$$
 (15)

$$CH_2OOH \rightarrow HCHO + OH$$
 (16)

OH radicals react 170 times more rapidly with benzene than with methane¹⁵ and so will preferentially attack benzene, causing an enhancement of the benzene decay. As the irradiation proceeds, oxidation products of CH₄ and benzene increase in concentration and compete for the available OH radicals, causing a decrease in benzene loss at longer irradiation times. We believe such complications explain the anomalous behavior we observe following irradiation of benzene/CH₄/Cl₂/air mixtures. Additionally, such complications would explain why, in the relative rate study of Atkinson and Aschmann,¹⁶ in air diluent, a rate constant $k_{12} = (1.5 \pm 0.9) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ is reported, which is at least 4 orders of magnitude greater than our value of $k_{12} < 5 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹.

The value of $k_6 = (6.1 \pm 0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ measured in the present study is in agreement with the two previous measurements of this rate constant: $(5.89 \pm 0.36) \times 10^{-11}$ and $(5.59 \pm 0.28) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.¹⁷

It is interesting to note the dramatic difference in reactivity of Cl atoms toward benzene and toluene. Cl atoms attack toluene at least 5 orders of magnitude more rapidly than benzene. This observation is consistent with our observation that benzyl radicals are the major, if not exclusive, product following the reaction of Cl atoms with toluene. It should be noted that our results do not preclude the formation of a short-lived, weakly bound Cl atomtoluene adduct. The adduct, if formed, will have three possible fates: (i) decomposition to regenerate Cl + toluene, (ii) reaction with Cl₂ to give dichloromethylcyclohexadiene, or (iii) reaction with O_2 to give a peroxy radical. In experiments performed in N₂, the formation of benzyl chloride, benzyl dichloride, and benzaldehyde accounted for $94 \pm 9\%$ of the observed toluene loss, suggesting the adduct does not react with Cl₂. As seen in Figure 2, k_6 was independent of the O₂ concentration, suggesting that the adduct is not lost via reaction with O_2 . We conclude that if a chlorine atom-toluene adduct is formed, it rapidly decomposes to regenerate Cl atoms. In the rest of this paper it is assumed that reaction 6 produces benzyl radicals in 100% yield.

FTIR Product Study of the Self-Reaction of Benzylperoxy Radicals. A product study was performed to provide insight into the mechanism of the self-reaction of benzylperoxy radicals. The photolysis of toluene/Cl₂/O₂/N₂ mixtures was used to generate benzylperoxy radicals. Figures 3A,B shows typical spectra acquired before and after a 30-s irradiation of a mixture of 106 mTorr of toluene and 435 mTorr of Cl_2 in 700 Torr of air diluent. Comparison of Figure 3B with a reference spectrum of benzaldehyde given in Figure 3C shows benzaldehyde is a major product. The loss of toluene was 20.1 mTorr (19% of the initial concentration), and the yield of benzaldehyde was 8.3 mTorr. Subtraction of IR features attributable to toluene and benzaldehyde gives Figure 3D (note the 10-fold change in y-axis scale). Comparison of Figure 3D and the 3400-3800-cm⁻¹ portion of Figure 3B, with a reference spectrum of benzyl alcohol (3E), shows the presence of 2.4 mTorr of the alcohol. The product feature at 3580 cm⁻¹ in Figure 3B is characteristic of an O-H stretch in a hydroperoxide which is presumably attributable to $C_6H_5CH_2OOH$. The yield of this product was estimated by comparing the integrated absorption over the region 3560-3610 cm⁻¹ with that of a calibrated reference spectrum of C₂H₅OOH (Figure 3F). CO_2 was observed as a minor product (<5% molar yield) with a yield which increased with consumption of toluene, suggesting it is a secondary product. Variation of the O_2 partial



Figure 3. IR spectra taken before (A) and after (B) a 30-s irradiation of a mixture of 106 mTorr of toluene and 435 mTorr of Cl_2 in 700 Torr of air diluent. Panel C is a reference spectrum of 11 mTorr of benzaldehyde. Subtraction of toluene and benzaldehyde features from (B) gives (D) (note y-axis scale change). Panel E is a reference spectrum of 59 mTorr of benzyl alcohol. Panel F is a reference spectrum in the OO-H stretching region of 49 mTorr of C_2H_5OOH .



Figure 4. Plot of the observed yields of benzaldehyde, benzyl alcohol, and benzyl hydroperoxide versus the loss of toluene following the irradiation of mixtures of toluene and Cl_2 in 700 Torr of N_2/O_2 mixtures. The open symbols were obtained by tandem mass spectrometry analysis, and the close symbols are data derived by FTIR analysis. Solid lines are linear least-squares fits. For clarity, the data for benzaldehyde and the hydroperoxide have been shifted vertically by 4 and 2 units, respectively.

pressure over the range 15–700 Torr had no observable effect on the measured product yields.

Within the experimental uncertainties, the yields of all products $(CO_2 \text{ excepted})$ were independent of the toluene consumption (3-20%), suggesting that secondary attack of Cl atoms was not a major complication. Nevertheless, with the data available from Table 1 we are able to make small corrections for secondary attack of Cl atoms. These corrections were in the range 2–15% and have been applied to the data shown in Figure 4. Allowance was made for formation of benzaldehyde following Cl atom attack of benzyl alcohol.

In addition to FTIR spectroscopy, the formation of benzaldehyde was monitored using tandem mass spectromety (MS-MS) in a limited subset of the present experiments. Results from the MS-MS technique are given along with those from the FTIR method in Figure 4. In all cases the benzaldehyde analysis from the two techniques was in agreement (within 10%), providing further confidence in our experimental technique.

Linear least-squares analysis of the data in Figure 4 gives the following molar product yields: C_6H_5CHO , $41 \pm 4\%$; C_6H_5 -

CH₂OH, 15 \pm 3%; ROOH, 18 \pm 4%. The CO₂ yield was 5 \pm 2%. In these experiments we can then account for 75 \pm 12% of the carbon. Quoted errors are 2 standard deviations.

After subtracting features attributable to toluene, benzaldehyde, benzyl alcohol, HCl, CO₂, and the hydroperoxide feature at 3560–3610 cm⁻¹ from our product spectra, small residual unidentified absorptions at 1092, 1179, 1272, 1340, 1695, and 1756 cm⁻¹ and trace features at 746, 818, 881, and 996 cm⁻¹ remained. These features are ascribed to the hydroperoxide C₆H₃-CH₂OOH and one, or more, unidentified products.

When reaction mixtures were allowed to sit in the dark in the chamber for up to 30 min a slow decay of benzaldehyde, benzyl alcohol, and the hydroperoxide was observed. The loss of benzyl alcohol was most pronounced with 20% loss in 30 min. The losses of benzaldehyde and the hydroperoxide were approximately 5-10% in 30 min. The observed decay in the dark presumably reflects heterogeneous losses either on the chamber walls or possibly on aerosol particles. The typical irradiation periods used in this work were 15-60 s. The slow loss of products in the dark should not affect the yields of these species measured immediately after irradiation.

To gain further insight into the chemistry of the present system, a limited series of experiments were performed in which CH_3OH was added to reaction mixtures containing toluene and Cl_2 in 700 Torr of air. Methanol was added to generate HO_2 radicals via the following reactions

$$CH_3OH + Cl \rightarrow CH_2OH + HCl$$
 (17)

$$CH_2OH + O_2 \rightarrow HCHO + HO_2$$
 (18)

Following the UV irradiation of toluene/CH₃OH/Cl₂/air mixtures, an aerosol was formed in the chamber as evidenced by a shift in base line which was more pronounced at high frequecies. The maximum shift corresponded to an absorbance change of 0.6 units at 3700 cm⁻¹. Benzaldehyde was observed as a product in a yield of 25% and 17% in experiments using [CH₃OH] = 200 mTorr and initial concentration ratios of [CH₃OH]/[toluene] = 1 and 1.5, respectively. The hydroperoxide was tentatively identified by virtue of the feature at 3560–3610 cm⁻¹; however, reliable quantification was precluded by the large amount of noise in these spectra, presumably resulting from the aerosol generation. A significant, permanent degradation of IR throughput performance resulted after the formation of aerosol in the chamber which required dismantling of the system and replacement of all optical components. These experiments were not repeated.

Flash Photolysis Kinetic Study

Experiment. The experimental apparatus has been described in detail previously.¹⁸ Briefly, it consists of a 70-cm-long thermostated Pyrex cell which can be cooled by flowing a liquid refrigerant in an outer jacket or heated in an oven. The flash was generated by discharging two capacitors through external argon flash lamps. Radical concentrations were monitored by timeresolved UV absorption spectrometry from 220 to 300 nm. The analysis beam from a deuterium lamp passed twice through the cell and impinged onto a monochromator/photomultiplier unit. Individual experimental absorption curves were fed into a transient recorder and passed to a microcomputer for averaging and further data analysis. The gas mixtures were flowed through the cell and regulated by Tylan flow controllers. The mixture was renewed between consecutive flashes, so that no products could be photolyzed, yielding secondary products. As discussed below, this was particularly important as one of the products, benzaldehyde, has a strong UV absorption band in this wavelength region and reacts rapidly with chlorine atoms.



Figure 5. Time-resolved UV absorption signals: (a) decay trace of the benzylperoxy radical recorded at 250 nm; (b) buildup of the benzaldehyde recorded at 240 nm. T = 300 K, $[Cl_2] = 4.6 \times 10^{16}$ molecules cm⁻³; $[toluene] = 6.5 \times 10^{15}$ molecules cm⁻³; $[C_6H_5CH_2O_2]_0 = 1.2 \times 10^{14}$ molecules cm⁻³, in 760 Torr of air. Smooth lines are the results of simulations.

For the experiments, slowly flowing toluene/chlorine/air or nitrogen mixtures were flash photolyzed in the thermostated cell. To obtain toluene in the gas phase, nitrogen was bubbled through liquid toluene maintained at 0 °C. The concentration of chlorine (L'Air Liquide, 5% in nitrogen) was maintained in the range $(2-7) \times 10^{16}$ molecules cm⁻³ and was measured by its absorption at 330 nm ($\sigma = 2.56 \times 10^{-19}$ cm² molecule⁻¹).¹¹ Toluene (Aldrich 99+%, spectrophotometric grade), benzaldehyde (Aldrich, 99+%), and methanol (Aldrich, 99.97%) were used without further purification. Experiments were performed from 273 to 450 K, at 760 Torr, most of them in synthetic air, except those in which the oxygen concentration was varied.

The concentrations of toluene, methanol, and oxygen were chosen such that stoichiometric conversion of chlorine atoms into peroxy radicals (reactions 6 and 2) was very rapid (<10 μ s) compared to the time scale of their subsequent removal (several milliseconds). Typical concentrations of reactants were as follows (in molecules cm⁻³ units): toluene, (6.5–65) × 10¹⁴; chlorine, (2–7) × 10¹⁶; methanol, (1–15) × 10¹⁵; balance, 760 Torr of air, resulting in initial radical concentration of (0.45–2) × 10¹⁴ molecules cm⁻³.

The resulting decay traces were averaged, typically over 10– 40 shots. Kinetic simulations were performed by numerical integration and fitted to the decay traces using nonlinear leastsquares analysis. Unless otherwise stated, errors are 1 or 2σ and represent experimental scatter only.

Results. On flash photolysis of the precursor mixture, transient absorptions were observed in the wavelength region 220–300 nm, which we attributed to the benzylperoxy radical (Figure 5). Experiments could not be performed below 220 nm, because of the strong absorption of the toluene precursor in this region. In addition, a residual absorption corresponding to the formation of a stable product was observed at all wavelengths. The shape of the time-resolved optical density changed markedly with the monitoring wavelength. Below 245 nm, the residual absorption was much stronger than the initial postflash optical density due to the radical and the resulting profile increased with time (Figure 5b). At longer wavelengths, the residual absorption was weaker and the resulting profiles decreased with time (Figure 5a). The

 TABLE 2:
 UV Absorption Cross Sections for the Benzylperoxy Radical and for Other Species Involved in the Reaction Mechanism

	$\sigma/10^{-18} \mathrm{cm}^2 \mathrm{molecule}^{-1}$					
λ/nm	C ₆ H ₅ CH ₂ O ₂	HO ₂	benzaldehyde	toluene	CH₃OOH	H ₂ O ₂
220	7.85 ± 1.15	3.47	25.5	0.13	0.15	0.26
225	4.45 🗙 1.45	2.92	42.0	0.03		
230	4.80 ± 1.20	2.30	58.5	0.05	0.10	0.19
235	4.75 ± 0.70	1.79	69.0	0.08		
240	6.05 ± 0.60	1.22	56.5	0.16	0.06	0.12
245	6.75 ± 0.70	0.83	7.05	0.26		
250	6.75 ± 0.4	0.54	2.75	0.37	0.04	0.09
255		0.32	3.05	0.43		
260	5.15 ± 0.10	0.18	3.65	0.61		
270	3.30 ± 0.35		4.65	0.10		
280	2.55 单 0.30		4.10			
290	1.80 ± 0.10		2.10			
300	0.85 ± 0.05		1.65			

TABLE 3: Rate Constants k_3 for the Benzylperoxy (RO2)Self-Reaction as a Function of Temperature

T/K	$[RO_2]_0/10^{13}$ molecules cm ⁻³	$k_3 \times 10^{12} \text{ a/cm}^3$ molecule ⁻¹ s ⁻¹	no. of runs
273	9.10	13.4 ± 1.79	6
283	9.50	8.80	1
298	11.5	6.95 ± 1.55	7
323	7.20	6.65 ± 1.30	5
348	11.0	2.70 ± 0.55	8
360	13.5	2.50	1
398	9.30	1.95 ± 0.20	7
411	13.5	1.85	1
451	9.45	1.15 ± 0.25	7

^a For $\alpha = 0.4$ (see text).

wavelength dependence of the residual absorption closely matches the intense gas-phase spectrum of benzaldehyde in this spectral region. Measurements of the magnitude of the residual absorption showed that the yield of benzaldehyde, relative to the initial concentration of benzylperoxy radical, is $45 \pm 5\%$, in agreement with the FTIR study. The quoted error includes uncertainties in the UV absorption cross section of benzaldehyde and the initial radical concentrations generated by the flash.

When HO₂ was present in the system, for the investigation of reaction 4, the general features of the traces were the same. However, the signal-to-noise ratio was lower than in the absence of HO₂, since the total initial radical concentration was shared between $C_6H_5CH_2O_2$ and HO₂. HO₂ could not be monitored as its absorption, between 200 and 240 nm, was hidden by those of toluene and benzaldehyde.

As the absorption of the benzaldehyde product plays an important role in the analysis of experimental traces, reliable absorption cross sections were necessary. These were determined using our experimental setup by flowing nitrogen containing a calibrated concentration of benzaldehyde into the reaction cell. The values of cross sections used in simulations are given in Table 2 along with those of HO₂, C₆H₅CH₂OOH (assumed equal to those of CH₃OOH), H₂O₂, and toluene (to take into account the small base line shift due to its consumption).

UV Spectrum of the Benzylperoxy Radical. The UV spectrum of the benzylperoxy radical was derived from the wavelength dependence of the absorbance after the photolysis flash. As benzaldehyde reacts rapidly with atomic chlorine, it was important to renew completely the cell content between two shots, in order to avoid the formation of other absorbing species.

Because of the $250-\mu s$ postflash dead time of the detection system, a short extrapolation to t = 0 was necessary to obtain a true spectrum of the peroxy radical, which was not perturbed by absorptions of reaction products. In particular, the strong absorption of benzaldehyde below 245 nm may have significantly distorted the peroxy radical spectrum. Consequently, absorption cross sections in this wavelength range have large uncertainties.



Figure 6. UV absorption spectrum of the benzylperoxy radical.



Figure 7. Arrhenius plot for the rate constant k_3 of the benzylperoxy radical self-reaction. The solid line represents the best weighted fit to $A \exp(B/T)$.

However, at longer wavelengths, where most kinetic information was obtained, absorption of products was low enough to perform extrapolations without difficulty.

As the rate of product formation is dependent on the reaction mechanism, it was important to extrapolate the experimental traces by simulations using the complete reaction mechanism (see discussion), based on the results of the FTIR study.

The radical spectrum was placed on an absolute basis by calibrating the absorption cross section at 250 nm against those of methylperoxy or hydroperoxy radicals produced in the same conditions, by replacing toluene by methane $(2 \times 10^{18} \text{ molecules cm}^{-3})$ or by methanol $(1 \times 10^{15}-1.5 \times 10^{16} \text{ molecules cm}^{-3})$, respectively. The yields of CH₃O₂ and HO₂ were determined using σ (CH₃O₂,240 nm) = $4.55 \times 10^{-18} \text{ cm}^2$ molecule^{-1 1} and σ (HO₂,220nm) = $3.70 \times 10^{-18} \text{ cm}^2$ molecule^{-1,19,20} No systematic differences were noticed on using these two calibrations.

Five relative spectra were recorded near room temperature and were averaged. The resulting spectrum is shown in Figure 6, and absolute cross sections are listed in Table 2. Referring to the small temperature dependence of peroxy radical UV spectra under *ca.* 400 K,²⁰ the absorption cross sections listed in Table 2 were assumed constant in the whole temperature range of this study. Note that error bars below 240 nm are large, due to the strong absorption of benzaldehyde, as emphasized above.

This spectrum is similar to those of most alkylperoxy radicals, above 230 nm.^{1,2} It differs markedly, however, below 230 nm, where the absorption seems to increase sharply. This second absorption band can probably be assigned to the presence of the aromatic ring.

Determination of the Rate Constant of Reaction 3. For the reaction

$$C_6H_5CH_2O_2 + C_6H_5CH_2O_2 \rightarrow \text{products}$$
 (3)

All kinetic data were obtained from traces recorded at 250 nm. This wavelength gave the best conditions for analyzing the decay traces, since it corresponds to the maximum absorption of the benzylperoxy radical and to a minimum in the absorption spectrum of benzaldehyde. The residual absorption due to benzaldehyde was therefore much smaller than the initial absorption due to the benzylperoxy radical (see Figure 5a). More than 40 traces similar to that shown in Figure 5a were recorded at temperatures between 273 and 450 K. The initial radical concentration was varied from 0.45×10^{14} to 2.0×10^{14} molecules cm⁻³; no systematic dependence of k_3 was observed. The oxygen concentration was also varied from 3.2×10^{16} to 4.0×10^{18} molecules cm⁻³, with no apparent effect on the kinetics, in agreement with the end-product analysis.

The decay traces followed second-order kinetics, provided the residual absorption of benzaldehyde was taken into account. The analysis resulted in the following rate expression for k_{obs} :

$$k_{\rm obs} = (2.75 \pm 0.15) \times 10^{-14} \exp[(1660 \pm 125)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

giving $7.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

The real value of the rate constant, which generally differs from k_{obs} because of HO₂ production in the system, will be derived below by simulation of the complete reaction mechanism. The real values of k_3 , which do not differ significantly from k_{obs} , are given in Table 3, and the corresponding Arrhenius plot is shown in Figure 7.

The temperature range over which experiments could be carried out was limited to 273-450 K. Beyond these temperatures the experimental traces were representative of other behaviors of the system: below 273 K, a strong apparent decrease of the reaction rate and an increase of the residual absorption at 250 nm were observed. We interpreted these phenomena as a contribution of chlorine atom addition to the aromatic ring of toluene, since this reaction is expected to increase in importance on lowering temperature. However, we have no proof for this interpretation, and the result obtained below 273 K were discarded. The kinetic behavior above 450 K also indicated a change in the reaction mechanism. In particular, at 240 nm, the time-resolved absorption no longer reached the steady level corresponding to the buildup of benzaldehyde but increased continuously, indicating the occurrence of a chain reaction. We believe that this observation is caused by the thermal decomposition of $C_6H_5CH_2O_2$ radicals, leading to equilibration between C₆H₅CH₂O₂ and C₆H₅CH₂:

$$C_6H_5CH_2 + O_2 \Leftrightarrow C_6H_5CH_2O_2$$
 (2, -2)

At temperatures greater than 450 K, thermal decomposition of benzylperoxy radicals becomes appreciable, due to the low bond dissociation energy $D(C_6H_5CH_2-O_2)$ of 117 kJ mol⁻¹, recently measured in Bordeaux.²¹ The presence of small amounts of benzyl radicals complicates the interpretation of our experimental traces in two ways. First, benzyl radicals absorb strongly at our monitoring wavelength: $\sigma(250 \text{ nm}) = 1.0 \times 10^{-16} \text{ cm}^2$ molecule⁻¹. Second, benzyl radicals will react with Cl₂ in a chain reaction; see reactions 9–11. Experiments at temperatures above 450 K were not pursued within this work, but the equilibrium (2, -2) was investigated in a separate study.²¹

Determination of the Rate Constant of Reaction 4. By analogy to other alkylperoxy radicals,^{1,2} the reaction of $C_6H_5CH_2O_2$ with HO₂ radicals is expected to form the hydroperoxide. HO₂ radicals were generated as for the FTIR study, by adding methanol to the reaction mixture (reactions 17 and 18).

$$C_6H_5CH_2O_2 + HO_2 \rightarrow C_6H_5CH_2OOH + O_2 \qquad (4)$$

Since the UV absorption of the HO_2 radical occurs below 240 nm and overlaps with the strong absorptions of toluene and

TABLE 4: Rate Constants k_4 for the Reaction of the Benzylperoxy Radical with HO₂ as a Function of Temperature

	•		-
T/K	[Cl] ₀ /10 ¹⁴ a	$k_4 \times 10^{12 \ b}$	no. of runs
273	0.85	15.4 ± 0.28	2
283	1.20	7.08 ± 2.99	3
296	1.10	10.2 ± 1.70	4
300	1.35	10.9 🛳 3.16	14
341	1.20	6.98 ± 1.20	5
355	1.60	7.00 ± 1.92	4
359	1.55	5.11 ± 0.93	4
389	0.90	4.64 ± 0.53	3
411	1.40	3.18 ± 0.72	5
447	0.91	4.95 ± 0.86	3

Detailed Results at 296 K Showing the Expected and Optimized Values of $\beta = [HO_{2}]_{0}/[Cl]_{0}$ (See Text)

	······································	-10/10 (·
[Cl] ₀ /10 ¹⁴ a	β expected	β optimized	$k_4 \times 10^{12} b$
1.15	0.64	0.68	8.35
1.15	0.64	0.65	9.80
1.10	0.82	0.81	11.0
1.05	0.69	0.67	11.5

 a Total initial radical concentration/molecules cm^-3. b In cm^3 molecule-1 $\rm s^{-1}.$

benzaldehyde, it could not be monitored directly. We could not use the method adopted in our former studies of the $RO_2 + HO_2$ reactions^{22,23} where pairs of traces, recorded at wavelengths specific of each radical, were analyzed simultaneously. As above, the kinetic information was determined from the analysis of decay traces recorded at a single wavelength, 250 nm. The ratio of initial concentrations $\beta = [HO_2]_0/([C_6H_5CH_2O_2]_0 + [HO_2]_0)$ was determined from the concentration ratio [toluene]/[methanol] and the rate constants of the reaction of each of these precursors with chlorine atoms. Independently, the value of this ratio was optimized in the simulations of the experimental traces, the total initial radical concentration, $[Cl]_0 = [C_6H_5CH_2O_2]_0 +$ $[HO_2]_0$, being determined by a preliminary calibration. Both procedures gave values in agreement within 15% (see an example at 296 K in Table 4), showing the consistency of the data used in the model.

The rate expression was derived from the analysis of 48 traces obtained in the temperature range 273-450 K and in 760 Torr of air. The initial radical concentration was varied from 8.0×10^{13} to 1.6×10^{14} molecules cm⁻³ by changing the concentration of molecular chlorine. The ratio of the concentrations of C₆H₃-CH₂O₂ and HO₂ was also varied from 1 to 5, by varying the relative concentrations of toluene and methanol.

Experimental traces were analyzed with the complete reaction mechanism discussed in the following section and resulted in the rate expression

$$k_4 = (3.75 \pm 0.32) \times 10^{-13} \exp[(980 \pm 230)\text{K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

giving k_4 (298 K) = 1.0×10^{-11} cm³ molecule⁻¹ s⁻¹. The experimental results are summarized in Table 4, and the corresponding Arrhenius plot is shown in Figure 8.

Discussion

Reaction Mechanism. By analogy to the mechanism of other peroxy radical self-reactions,^{1,2} the self-reaction of benzylperoxy radicals is expected to proceed via two channels:

$$C_6H_5CH_2O_2 + C_6H_5CH_2O_2 \rightarrow C_6H_5CH_2O + C_6H_5CH_2O + O_2 (3a)$$

$$C_6H_5CH_2O_2 + C_6H_5CH_2O_2 \rightarrow C_6H_5CHO + C_6H_5CH_2OH + O_2 (3b)$$

with possibly a small contribution from a third channel:



Figure 8. Arrhenius plot for the rate constant k_4 of the benzylperoxy radical reaction with HO₂. The solid line represents the best weighted fit to $A \exp(B/T)$.

$$C_{6}H_{5}CH_{2}O_{2} + C_{6}H_{5}CH_{2}O_{2} \rightarrow C_{6}H_{5}CH_{2}OOCH_{2}C_{6}H_{5} + O_{2} (3c)$$

Dibenzyl peroxide is not available commercially, and we were unable to acquire a reference spectrum of this compound. Some of the small residual unidentified FTIR features observed in the product spectra could be tentatively assigned to the peroxide, ROOR, but the lack of characteristic absorption bands of the peroxidic O-O bond in organic peroxides precludes any definitive identification.

The observation of benzyl alcohol as a product shows that channel 3b is significant. The difference in the observed yields of benzaldehyde and benzyl alcohol shows that channel 3a is also important. Channel 3a produces the alkoxy radical $C_6H_5CH_2O$. This alkoxy radical will either react with O_2 to give benzaldehyde, decompose via C-C bond fission to give a phenyl radical and HCHO, or decompose via ring opening. The fact that the observed benzaldehyde yield is 3 times that of benzyl alcohol shows that reaction with O_2 is an important fate of $C_6H_5CH_2O$ radicals. The invariance of the benzaldehyde yield with the O_2 partial pressure over the range 15-700 Torr, as well as the kinetic behavior, suggests that reaction with O2 is the exclusive fate of C6H5CH2O radicals. Additional evidence to support this notion comes from the absence of HCHO as an observed product, indicating that C-C bond fission is unimportant. We conclude that reaction 19 is the sole fate of $C_6H_5CH_2O$ radicals.

$$C_6H_5CH_2O + O_2 \rightarrow C_6H_5CHO + HO_2$$
(19)

 HO_2 radicals formed in reaction 19 are expected to react with other HO_2 radicals or with benzylperoxy radicals or both:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{20}$$

$$HO_2 + C_6H_5CH_2O_2 \rightarrow C_6H_5CH_2OOH + O_2 \qquad (4)$$

Our data permit an assessment of the relative branching ratio $k_{3a}/k_{3b} = [(yield of benzaldehyde) - (yield of benzyl alcohol)]/(twice the yield of benzyl alcohol) = <math>0.9 \pm 0.3$, i.e., approximately unity. The quoted error reflect uncertainties in both the measured benzaldehyde and alcohol yields and was calculated using conventional propagation of error analysis.

If reaction 3 proceeded solely through channels 3a and 3b, the yield of benzaldehyde would be expected to be 50% or greater (depending on the relative efficiency of reactions 20 and 4 as sinks for HO₂ radicals). The observed yield of benzaldehyde is $41 \pm 4\%$, suggesting that channel 3c may contribute to the overall reaction. At the present time, in the absence of a reference spectrum for benzyl peroxide, we tentatively ascribe a branching ratio $k_{3c}/k_3 = 0.2$. Any other unidentified terminating reaction channel would be equivalent to channel 3c. This uncertainty on

TABLE 5: Reaction Mechanism ($R = C_6H_5$)

reaction	rate constant ^a (300 K)	reference
$\frac{1}{Cl_2 + h\nu \rightarrow Cl + Cl}$		
$Cl + toluene \rightarrow RCH_2 + HCl$	6.1 × 10 ⁻¹¹	this work
$RCH_2 + O_2 + M \rightarrow RCH_2O_2 + M$	1.1 × 10 ^{-12 b}	7
$\frac{\text{RCH}_2\text{O}_2 + \text{RCH}_2\text{O}_2 \rightarrow \text{RCH}_2\text{O} + \text{RCH}_2\text{O} + \text{RCH}_2\text{O} + \text{O}_2}{\text{RCH}_2\text{O} + \text{O}_2}$	3.0×10^{-12}	this work
$\frac{\text{RCH}_2\text{O}_2 + \text{RCH}_2\text{O}_2 \rightarrow \text{RCH}_2\text{CHO} + \text{RCH}_2\text{OH} + \text{O}_2}{\text{RCH}_2\text{OH} + \text{O}_2}$	3.0×10^{-12}	this work
$\begin{array}{c} \text{RCH}_2\text{O}_2 + \text{RCH}_2\text{O}_2 \rightarrow \\ \text{RCH}_2\text{OOCH}_2\text{R} + \text{O}_2 \end{array}$	1.5×10^{-12}	this work
$RCH_{2}O + O_{2} \rightarrow RCHO + HO_{2}$ $RCH_{2}O_{2} + HO_{2} \rightarrow RCH_{2}OOH + O_{2}$ $HO_{2} + HO_{2} \rightarrow H_{2}O_{2} + O_{2}$	1.9 × 10 ⁻¹⁵ 9.9 × 10 ⁻¹² 3.0 × 10 ⁻¹²	11 this work 11

^a Units of cm³ molecule⁻¹ s⁻¹. ^b Assumed equal to methyl analog.

the reaction mechanism has been taken into account below in the overall uncertainties on rate constants.

The observation of a significant hydroperoxide yield in the FTIR study shows that reaction of benzylperoxy radicals with HO₂ is important. To compete with the rapid self-reaction of benzylperoxy radicals observed in this work, reaction 4 must also proceed rapidly. A crude estimate for k_4 can be derived by modeling the system using the Acuchem kinetic modeling program²⁴ with the chemical mechanism given in Table 5. In this mechanism we assume a 20% contribution by channel 3c, with $\alpha = k_{3a}/k_3 = k_{3b}/k_3 = 0.4$. This is in good agreement with the value of 0.36 recently found by Seuwen and Warneck.²⁵ With k_4 fixed at 1, 5, 10, and 50 × 10⁻¹² cm³ molecule⁻¹ s⁻¹, the ROOH yields are predicted to be 6, 18, 23, and 28%, respectively. Within the combined experimental uncertainties, the observed yield of $18 \pm 4\%$ is consistent with the value of $k_4 = (1.02 \pm 0.13) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ measured using the flash-photolysis system.

UV Absorption Spectrum of the Benzylperoxy Radical. As emphasized above, the time-resolved traces could only be correctly extrapolated to the origin if they were fitted using the complete reaction mechanism with the appropriate rate constants. However, at 250 nm, the absorption is almost entirely due to the $C_6H_5CH_2O_2$ radical, and therefore, the extrapolation was insensitive to the reaction mechanism used. Even when fitting the decay traces with simple second-order kinetics, slightly corrected for the small absorption of benzaldehyde, a correct value for the absorption cross section was obtained. Thus, the kinetics could be determined at 250 nm and used for a reliable determination of the UV absorption spectrum in the explored spectral range. It should be emphasized that there are larger uncertainties associated with the cross section values at wavelength below 245 nm, due to interferences caused by the strong benzaldehyde absorption.

The principal absorption band that could be characterized peaks at 245 nm and is similar to the well-known UV spectra of alkylperoxy radicals,^{1,2} with a slightly higher absorption cross section at the maximum. The beginning of a second stronger absorption band is clearly evident at shorter wavelengths. This band indicates the occurrence of a coupling between the O–O[•] chromophore and the π system of the aromatic ring, even if the two chromophores are separated by a saturated carbon atom. This is to be compared to the spectrum of the acetylperoxy radical, which also exhibits two similar absorption bands, revealing a coupling between the peroxy group and the π electrons of the carbonyl group.

Determination of the Rate Constants k_3 and k_4 . It should be noted that the value of k_{obs} derived in our study of the self-reaction of benzyl peroxy radicals is an overestimate of the "true value" of the bimolecular rate constant. This is due to the production of HO₂ radicals and their secondary reaction with benzylperoxy radicals to give the hydroperoxide. The true value for k_3 can be determined by simulating the decay traces using the complete reaction mechanism. As emphasized above, only the traces obtained at 250 nm were used for deriving the kinetic data. The traces recorded at 240 nm near the maximum absorption of benzaldehyde were useful, however, to assess the consistency between the kinetics and the reaction mechanism. In particular, these traces allow us to determine a benzaldehyde yield of $45 \pm 5\%$, in excellent agreement with that determined in the FTIR study. At the same time, the kinetics of the buildup of the benzaldehyde absorption was correctly reproduced using the kinetic parameters determined at 250 nm, as shown in Figure 5b.

The analysis of the kinetics is expected to be sensitive to the value of the branching ratio α , since channel 3a results in the formation of HO₂ radicals (by reaction 19), which subsequently react with C₆H₃CH₂O₂ radicals. The room temperature data were analyzed using $\alpha = k_{3a}/k_3 = 0.4$, $k_{3b}/k_3 = 0.4$, and $k_{3c}/k_3 = 0.2$, as suggested by the results of the FTIR study. The fact that the small residual absorption at 250 nm was consistent with the yield and absorption cross section of benzaldehyde showed that no other absorbing species contributed significantly to the signal. In particular, the peroxide C₆H₅CH₂OOCH₂C₆H₅, if formed, absorbs too weakly at this wavelength to be detected.

All traces were well fit using the above branching ratios and resulted in a set of values for k_3 and k_4 . As the values of k_3 and k_4 are similar, their values obtained from simulations of decay traces were almost insensitive to the value of α . The room temperature rate constant obtained is $k_3 = (6.9 \pm 1.5) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, which is not much different from k_{obs} .

Generally, for alkylperoxy radicals, it is observed that $\alpha =$ k_{3a}/k_3 increases with temperature and becomes nearly equal to unity above ca. 500 K. Unfortunately, the end-product analyses could only be performed at room temperature and could not provide any temperature dependence for this parameter. Since the yield of benzaldehyde depends on the value of α , values of the benzaldehyde yield obtained from experimental traces recorded at different temperatures should have provided a determination of the temperature dependence of α . However, the expected variations of the benzaldehyde yield were of the order of the uncertainties on $\sigma_{\text{benzaldehyde}}$, and in addition, they were almost insensitive to α in the simulations. Indeed, the increase of the yield of benzaldehyde with α (reactions 3 and 19) is compensated by the reduction of the overall yield due to a larger production of HO₂ (reaction 19), which consumes benzylperoxy radicals (reaction 4). It should be noted that monitoring the absorption of HO₂ around 210-220 nm, which could also have provided a good estimation of α variations, was not possible because of the strong absorption of benzaldehyde and toluene at these wavelengths.

Since, in this particular case, k_3 is insensitive to the value of α , we have performed a first analysis of the data, using $\alpha = 0.4$ at all temperatures. The resulting rate constants, collected in Table 4, yield the following rate expression:

 $k_3 = (2.75 \pm 0.15) \times 10^{-14} \exp[(1680 \pm 140)\text{K}/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

In addition, to test the error that would result from a significant temperature dependence of α , the data obtained at the highest temperatures of the flash-photolysis experiments, *i.e.*, from 360 to 450 K, were analyzed with $\alpha = 0.8$, estimated from the temperature dependences of the branching ratios observed for other peroxy radicals.^{1,2} The resulting values of k_3 changed by no more than 5%, which is much smaller than the experimental uncertainties. The above expression can thus be taken as a good representation of the temperature dependence of k_3 .

The quoted uncertainties on the expressions of k_3 and k_4 correspond to the statistical dispersion of data (1 σ). However, additional systematic errors should be taken into account. The main sources of such errors are the uncertainties on absorption cross sections and on the reaction mechanism, as discussed below.

As noted above, the value of k_3 derived from our analyses is insensitive to the value of α , due to the relatively small difference between the rate constants of reactions 3 and 4. Therefore, the uncertainty on α does not contribute significantly to the uncertainty in k_3 and k_4 . However, the unidentified products may contribute to the reaction mechanism and to the UV absorption, thus resulting in errors in the kinetic analysis. We believe that this possibility is unlikely, as the UV absorption traces could correctly be accounted for at all wavelengths by the identified products. This provides a good indication that the unidentified products are molecular species (radical species generally absorb in the explored UV spectral range), which do not contribute to the chemistry. We estimate that the overall uncertainty on the values of k_3 is around 50%.

Determination of the initial RO_2 and HO_2 radical concentrations is the largest potential source of uncertainty in k_4 . Two independent methods were employed to measure $[RO_2]_0$ and $[HO_2]_0$. It was shown that the results from both method were in excellent agreement (within 15%), giving us confidence in our measured values of $[RO_2]_0$ and $[HO_2]_0$. We estimate that the overall uncertainty in k_4 is also approximately 50%.

Reactivity of the Benzylperoxy Radical Compared to That of of Other Peroxy Radicals. The rate constant obtained for the self-reaction of the benzylperoxy radical must be compared to that of primary peroxy radicals, since the self-reactions of secondary and tertiary peroxy radicals exhibit positive activation energies, indicating a different reaction mechanism. Among primary peroxy radicals whose reaction kinetics have been investigated to date, the self-reactions of methyl- and ethylperoxy radicals are the slowest.^{1,2} Chlorine-substituted and OHsubstituted methyl- and ethylperoxy radicals, radicals bearing particular functions like acetylperoxy $(CH_3C(O)O_2)$ or acetonylperoxy radicals $(CH_3C(0)CH_2O_2)$, and large radicals like neopentylperoxy radicals exhibit much faster self-reactions. The results obtained in this work for the benzylperoxy radical are in line with these trends. This reaction is among the fastest, with a rate constant approaching 10-11 cm³ molecule⁻¹ s⁻¹ at low temperature. It can be concluded that the aromatic substituent does not bring any specificity in the reactivity of peroxy radicals since the effect is analogous to that of the other substituents mentioned above.

The negative temperature coefficient and the value of α which is close to that measured for other alkylperoxy radicals suggest that the reaction mechanism is similar to that of self-reactions of other peroxy radicals;^{1,2} reaction proceeds through a stable tetroxide intermediate, which can decompose in different ways, corresponding to channels 3a, 3b, and 3c. The end-product analysis was able to identify $75 \pm 12\%$ of the products following the self-reaction of benzyl peroxy radicals. Clearly, one or more unidentified products were formed. We have assumed in the analysis of the present results that the principal unidentified product was the dibenzyl peroxide formed in reaction channel 3c. Further end-product analyses are necessary to resolve this point since, so far, this reaction channel has never been characterized.

Previous work from our laboratory has shown that large peroxy radicals such as $c-C_5H_9O_2$, $c-C_6H_{11}O_2$, and $(CH_3)_3CCH_2O_2$ react rapidly with HO₂ radicals with rate constants in the range $(1.5-1.8) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 298 K.²⁶ In the present work we show that benzyl peroxy radicals also react rapidly with HO₂ radicals with a room temperature rate constant of 1.0×10^{-11} cm³ molecule⁻¹ s⁻¹. The reaction of benzyl peroxy with HO₂ radicals displays a significant negative temperature dependence comparable in magnitude to that previously reported for other peroxy radical reactions.^{1,2}

Atmospheric Implications. The aim of the present study is to improve our understanding of the atmospheric chemistry of peroxy radicals and thereby facilitate an accurate representation of these species in computer models of atmospheric processes. We show here that benzyl peroxy radicals react rapidly with HO₂ radicals, $k_4 = 1.0 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 296 K. As discussed previously,²⁶ atmospheric modelers currently use values of (3-5) $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ for the generic reaction of RO₂ + HO₂. In light of the present work and previous studies in our laboratory,²⁶ a value of (1.0-1.5) $\times 10^{-11}$ cm³ molecule⁻¹ s1-1 seems more appropriate for large peroxy radicals derived form non-methane hydrocarbons.

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