Study of a Benzoylperoxy Radical in the Gas Phase: Ultraviolet Spectrum and $C_6H_5C(O)O_2$ + HO₂ Reaction between 295 and 357 K

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This work reports the ultraviolet absorption spectrum and the kinetic determinations of the reactions $2C_6H_5C(O)O_2 \rightarrow \text{products}$ (I) and $C_6H_5C(O)O_2 + HO_2 \rightarrow C_6H_5C(O)O_2H + O_2$ (IIa), $\rightarrow C_6H_5C(O)OH + O_3$ (IIb), $\rightarrow C_6H_5C(O)O + OH + O_2$ (IIc). Experiments were performed using a laser photolysis technique coupled with UV-visible absorption detection over the pressure range of 80-120 Torr and the temperature range of 293-357 K. The UV spectrum was determined relative to the known cross section of the ethylperoxy radical $C_2H_5O_2$ at 250 nm. Kinetic data were obtained by simulating the temporal behavior of the UV absorption at 245-260 nm. At room temperature, the rate constant value of reaction I (cm³ · molecule⁻¹ · s⁻¹) was found to be $k_I = (1.5 \pm 0.6) \times 10^{-11}$. The Arrhenius expression for reaction II is (cm³ · molecule⁻¹ · s⁻¹) $k_{II}(T) = (1.10 \pm 0.20) \times 10^{-11} \exp(364 \pm 200/T)$. The branching ratios β_{O3} and β_{OH} , respectively, of reactions IIb and IIc are evaluated at different temperatures; β_{O3} increases from 0.15 \pm 0.05 at room temperature to 0.40 \pm 0.05 at 357 K, whereas β_{OH} remains constant at 0.20 \pm 0.05. To confirm the mechanism of reaction II, a theoretical study was performed at the B3LYP/6-311++G(2d,pd) level of theory followed by CBS-QB3 energy calculations.

I. Introduction

Benzaldehyde is the most abundant oxygenated aromatic compound found in the polluted urban air.¹ As with other aromatic hydrocarbons, the contribution of benzaldehyde to problems of urban air pollution, such as formation of ozone as well as of secondary aerosol,^{1,2} is well recognized. This compound is widely emitted in the atmosphere as a primary pollutant from both natural and anthropogenic sources. The main natural sources of benzaldehyde are emissions from vegetation, volcanic eruption, and so forth.^{3,4} In addition, it is used in several industrial sectors such as the pharmaceutical industry and in manufacturing solvents, flavors, and perfumes.⁵⁻⁷ It is also produced from the incomplete combustion of automobile fuels.8 Moreover, benzaldehyde is formed in the atmosphere, as a secondary pollutant, from several aromatic compounds.^{1,9-11} Considering these numerous sources of this species, extensive progress has been made toward the knowledge of the atmospheric chemistry of benzaldehyde. Most of the results concerning these species were summarized in other references.^{1,9,10} However, significant uncertainties remain. In particular, the reactivity of aromatic radicals, such as the benzoylperoxy radical, an important intermediate species in the atmospheric oxidation processes of benzaldehyde, continues to be vague. In the troposphere, the potential removal processes of benzaldehyde are mainly photolysis and chemical reactions with OH, Cl, and NO₃ radicals.^{1,9,10,12–15} These chemical reactions proceed mainly by the acyl H abstraction, leading to the benzoylperoxy radical in an excess of O_2 . In the present paper, we report the following results:

the UV absorption spectrum of the benzoylperoxy radical the kinetics of the following reactions

$$2C_6H_5C(O)O_2 \rightarrow \text{products}$$
 (I)

$$C_6H_5C(O)O_2 + HO_2 \rightarrow products$$
 (II)

For the reaction I, only one determination¹⁶ of the rate constant and one determination of the $C_6H_5C(O)O_2$ UV spectrum are available in the literature. We provide a second determination of the kinetic rate constant of the self-reaction I at room temperature using laser photolysis. Concerning reaction II, this type of reaction is well-known to play an important role in the atmospheric oxidation process of volatile organic compounds in the regions where the concentration of NO_x is weak. As far as we know, for reaction II, no kinetic determinations are available. This reaction may proceed via three channels

$$C_6H_5C(O)O_2 + HO_2 \rightarrow C_6H_5C(O)O_2H + O_2$$
 (IIa)

$$C_6H_5C(O)O_2 + HO_2 \rightarrow C_6H_5C(O)OH + O_3$$
 (IIb)

$$C_6H_5C(O)O_2 + HO_2 \rightarrow C_6H_5C(O)O + OH + O_2$$
(IIc)

Channel IIb leads to O₃. One focus of the paper is therefore to discuss the impact of benzaldehyde in tropospheric ozone formation by the determination of the branching ratio $\beta_{O3} =$

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 $k_{\rm IIb}/k_{\rm II}$. Channel IIc has received particular attention for otherperoxyl radicals, mainly the acetylperoxyl.^{17,18} Recently, Dillon and Crowley¹⁹ and Jenkin et al.²⁰ discussed the occurrence of channel IIc for the acetylperoxyl radical. Dillon and Crowley¹⁹ concluded that OH was significantly observed for carbonylcontaining RO₂. However, the radical OH is not easy to detect. Some studies use indirect detection by adding benzene in the reaction mixture to scavenge OH and form phenol.^{18,20} Dillon and Crowley¹⁹ provide direct measurement by laser-induced florescence. Hasson et al.²¹ propose a theoretical study.

Only few data are available for the benzoylperoxyl radical. Recently, Dillon and Crowley¹⁹ pointed out "strong evidence" of OH formation with β_{OH} values of about 0.2 at room temperature. Thus, to enrich kinetic data concerning this compound, we have undertaken the study of this species. The experimental technique used in this work was laser photolysis with time-resolved absorption UV-visible spectroscopy. Moreover, to confirm the mechanism of reaction II, a theoretical study was performed at the B3LYP/6-311++G(2d,pd) level of theory followed by CBS-QB3 energy calculations.

II. Experimental Section

1. Experimental Apparatus. The experimental device has been described previously.²² Therefore, it will only be briefly described here. The setup of the laser photolysis/UV absorption device consists of a double-jacket Pyrex cell (56 cm in length and 2.5 cm in diameter), equipped with quartz windows. A circulating fluid between the inner wall and the second jacket regulates the temperature. An excimer laser (Lambda-Physik COMPex 201) operating at 351 nm provides the photolysis pulse. The laser produces 40 ns pulses with energies ranging from 160 to 300 mJ at a maximum repetition rate of 10 Hz. A computer commands the trigger pulse of the laser. The beam emerging from a deuterium lamp passes the reaction cell and is analyzed by a Jobin Yvon monochromator (focal length: 245.76 mm; aperture F/4; blazed grating: 1200 lines/mm; dispersion: 3 nm/mm; resolution: 0.1 nm) and a R928 Hamamatsu photomultiplier. Data are transferred to the microcomputer for storage. To improve the signal-to-noise ratio of the recorded data, the signal intensity versus time profiles are averaged over 300-1000 laser shots for each studied wavelength.

Calibrated gas flow controllers maintain steady gas flows. All flow rates are measured with mass flow meters calibrated by measuring the rate of pressure increase in a known volume. A 0-1000 mbar MKS Baratron capacitance manometer measures the pressure in the reactor, and two sensors give the temperature inside the cell.

2. Experimental Conditions. The benzoylperoxy radical is generated by photolysis of a slow-flowing Cl₂, N₂, O₂, C₆H₅CHO mixture via the following reactions

$$C_1 + C_6 I_5 C_{10} + C_6 I_5 C_{10} + I_1 C_1$$
 (III)

$$C_6H_5CO + O_2 + M \rightarrow C_6H_5C(O)O_2 + M$$
 (IV)

As explained in ref 16 reaction III proceeds entirely by H abstraction to form benzoyl radical in 100% yield.

To study reaction II, methanol was added to generate hydroperoxy radical as follows

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

$$CH_2OH + O_2 \rightarrow CH_2O + HO_2$$
 (VI)

To quickly convert the chlorine atoms, minimize secondary reaction effects, and avoid product accumulation, the initial C_6H_5CHO concentration must be a few orders of magnitude lower than that of O_2 and at least equivalent to the initial concentration of Cl_2 , $[O_2] \gg [Cl_2] \approx [C_6H_5CHO]$). Benzalde-hyde and methanol were premixed with nitrogen in a 10 L glass bulb to form a 0.5–1.2% mixture at a total pressure of about 1000 Torr. The O_2 concentration was calculated from the mass flow rate, the temperature, and the pressure in the reaction cell. Accurate measurements of Cl_2 and benzaldehyde concentrations were obtained by measuring the absorption of Cl_2 at 330 nm ($\sigma_{Cl2} = 2.55 \times 10^{-19}$ molecule⁻¹·cm^{2 23}) and the absorption of benzaldehyde at 260 nm ($\sigma_{benzaldehyde} = 1.3 \times 10^{-18}$ molecule⁻¹·cm^{2 22}). During an experiment, the variation of the concentration did not exceed 15%.

All experiments were performed within the following range of initial conditions: temperature, 293–357 K; pressure, 80–120 Torr; optical path, 56 cm. To obtain more accurate results, experimental conditions were widely varied, particularly the initial total concentrations (cm³·molecule⁻¹) of RO₂ and HO₂ and the ratio (methanol/toluene), which were varied from 1.0 × 10¹⁴ to 5.0 × 10¹⁴ and 0 to 4, respectively. These variations were accomplished by varying the chlorine, benzaldehyde, and methanol concentrations and the laser energy. The reagent concentrations were (molecule·cm⁻³) [Cl₂] = (1.0–10) × 10¹⁵, [O₂] = (0.5–2) × 10¹⁸, [C₆H₅CHO] = (0.5–1.0) × 10¹⁵, and [CH₃OH] = (0.0–5.0) × 10¹⁵. Under these conditions, the concentrations of the intermediate absorbing species were about (1.0–5.0) × 10¹⁴ molecule·cm⁻³.

The reagents used were obtained from the following sources: Cl_2 (1% in N₂ pure), O₂ (99.999% pure), and C_2H_6 (99.999% pure) were provided by Air Liquide and benzaldehyde (99.8%) and methanol (99.8%) were provided by Aldrich. All of the reagents were used without further purification.

III. Temporal Profile Analysis: Method

1. Determination of the Benzoylperoxy Spectrum. The cross section values of the benzoylperoxy radical were determined relative to the absorption cross section of $CH_3CH_2O_2$ at 250 nm, which is fairly well-known, $\sigma_{250,C2H5O2} = 4.12 \times 10^{-18}$ cm²·molecule⁻¹,²⁴ using the procedure described in ref 22. Cross sections were determined by analyzing experiments when no methanol was added in the flashed mixture to avoid reaction II. In each set of experiments, the benzaldehyde was replaced in the gas mixture by C_2H_6 using the same experimental conditions (chlorine concentration, laser energy, pressure, etc.); the initial concentration of the peroxy radical was determined from these experiments. Thus, the ratio of the initial optical densities (ODs) allows the calculation of the benzoylperoxy cross section according to the relation

$$\frac{\sigma_{\lambda,\text{RO2}}}{\sigma_{250,\text{C2H5O2}}} = ([\text{OD}]_{\lambda,\text{RO2}})_0 / ([\text{OD}]_{250,\text{C2H5O2}})_0$$
(1)

where $\sigma_{\lambda,RO2}$ is the absorption cross section of the benzoylperoxy radical at the wavelength λ and ([OD]_{$\lambda,RO2$})₀ and ([OD]_{250,C2H5O2})₀ are the initial ODs of benzoylperoxy and ethylperoxy radicals, respectively. These parameters were obtained by extrapolating

TABLE 1: Cross Sections of the Benzoylperoxy Radical and of the Benzoic Acid $(10^{-18} \text{ cm}^2 \cdot \text{molecule}^{-1})$

wavelength (nm)	C ₆ H ₅ C(O)O ₂	C ₆ H ₅ CO ₂ H
220	24.5 ± 5.3	1.95 ± 0.19
225		2.39 ± 0.23
230		2.93 ± 0.71
235		1.62 ± 0.14
240		0.87 ± 0.15
245	12.4 ± 1.0	0.63 ± 0.14
250	13.0 ± 2.2	0.64 ± 0.15
255	11.2 ± 1.8	0.67 ± 0.15
260	9.2 ± 0.2	0.73 ± 0.15
265		0.83 ± 0.17
270	6.0 ± 0.7	0.89 ± 0.17
275		0.64 ± 0.08
280	3.5 ± 1.2	0.49 ± 0.05

the first points of the signal OD = f(t) to t = 0, for which the main species absorbing is the studied RO₂ radical. The absorption of other species is neglected.²² Several determinations of cross section values were done per wavelength.

2. Kinetic Determinations and Mechanistic Scheme. *Temporal Optical Density Profile Analysis*. The OD recorded during an experiment results from the absorption of several species corresponding to a time-dependent total OD, such that

$$(OD)_{\lambda,\text{total}} = \sum (OD)_{\lambda,i} = f(t)$$
 (2)

Here, i is $C_6H_5C(O)O_2$, H_2O_2 , HO_2 , C_6H_5CHO , C_6H_5 , $C_6H_5O_2$, C_6H_5O , C_6H_5COCl , C_6H_5OCl , $(C_6H_5)_2O$, $(C_6H_5)_2O_2$, O_3 , $C_6H_5C-(O)OH$ and $C_6H_5C(O)O_2H$.

The OD is related to the concentration according to Beer-Lambert's law

$$(OD)_{\lambda i} = \sigma_{\lambda i} l C_i \tag{3}$$

where *l* is the optical path, $\sigma_{\lambda,i}$ the absorption cross section at the wavelength λ for the species i, and *C*_i the concentration.

The total OD is recorded in the spectral range of 245-260 nm. Below 245 nm, benzaldehyde, as well as the stable products resulting from the photolysis, has a strong absorption, inducing errors in kinetic determinations. Moreover, the cross sections of some products (C₆H₅COCl) and intermediate radical species (C₆H₅, C₆H₅O₂) are not known at low wavelengths. Above 260 nm, the OD is too low to provide accurate determination. At 250 nm, the absorption of the benzoylperoxy radical is important relative to the other absorbing species, and the absorption of benzaldehyde is low. Hence, experimental data obtained at this wavelength were used to extract kinetic parameters. The signals obtained at 245, 255, and 260 nm.

The exploitation of the temporal OD signal implies an accurate knowledge of absorption cross sections. The absorption cross section values of $C_6H_5C(O)O_2$ derived from the present study are listed in Table 1. The absorption cross section values of $C_6H_5C(O)OH$ were measured in our laboratory by means of the experimental device described previously²⁵ (Table 1). $C_6H_5C(O)O_2H$ cross sections have been set by analogy, regarding that $CH_3C(O)O_2H$ cross sections are about 2.5 times higher than the ones of $C_6H_5C(O)O_2H$ about 10 times lower than cross

TABLE	2: Cross	Sections	of Absorbing	Species	at	the
Studied	Waveleng	th (10^{-18})	cm ² ·molecule	-1)		

species/ wavelength (nm)	245	250	255	260	ref
H_2O_2	0.10	0.08	0.06	0.05	23
HO ₂	0.80	0.48	0.26	0.13	24
C ₆ H ₅ CHO	2.08	1.30	0.92	1.25	22
C_6H_5	20.0	27.5	21.0	15.0	47
$C_6H_5O_2$	1.50	2.0	2.00	2.50	27
C ₆ H ₅ O	11.0	6.3	4.90	3.60	29
C ₆ H ₅ COCl	0.75	1.9	1.60	2.60	16
C ₆ H ₅ OCl	0.70	1.2	1.60	2.30	27
$(C_6H_5)_2O$	0.03	0.04	0.05	0.07	estimated
$(C_6H_5)_2O_2$	4.7	3.4	3.1	4.0	27
O ₃	9.5	10.8	11.3	10.8	46
C ₆ H ₅ C(O)O ₂ H	1.2	1.2	1.1	0.9	by analogy with CH ₃ C(O)O ₂ H

sections of the benzoylperoxyl radical. Cross sections of other absorbing species were taken from literature (see references in Table 2).

Mechanism Scheme. Owing to the complex nature of the chemical system, simulations of our experiments were performed to extract kinetic parameters. The reaction scheme used is presented in Table 3. This kinetic model involves the main processes occurring during the photolysis of the mixture $Cl_2/C_6H_5CHO/CH_3OH/O_2/N_2$. It includes reactions producing and consuming $C_6H_5C(O)O_2$ and HO_2 . A few other secondary reactions were added according to data from previous studies (see references in Table 3). In this reaction scheme, we can note the following:

• By analogy with the $CH_3C(O)O_2$ self-reaction, the $C_6H_5C(O)O_2$ self-reaction is assumed to produce $C_6H_5C(O)O$, which decomposes instantaneously into the benzyl radical and carbon dioxide.¹⁶ According to refs 27 and 28, the fate of C_6H_5 proceeds mainly via its reaction with O_2 to form $C_6H_5O_2$.

• Channels IIa and IIb lead to stable products. On the contrary, channel IIc is a propagation channel. It leads either to the formation of C_6H_5 and $C_6H_5O_2$ via reactions VII and IX or feeds back, via reaction VIII, into the pathways IIa and IIb, leading to O_3 , benzoic acid, and peroxy benzoic acid

$$C_6H_5CHO + OH \rightarrow C_6H_5C(O) + H_2O$$
 (VIII)

Furthermore, $C_6H_5C(O)$ reacts with O_2 to generate the benzoylperoxyl radical $C_6H_5C(O)O_2$ via reaction IV (Table 3). The formation of additional HO₂ can be explained by this system

$$CH_3OH + OH \rightarrow CH_2OH + H_2O$$
 (XX)

$$CH_2OH + O_2 \rightarrow CH_2O + HO_2$$
 (VI)

During the simulation, rate constants of reactions I and II and branching ratio were varied until obtaining the best agreement between simulation and experimental data.

Sensitivity Analysis. A detailed kinetic sensitivity analysis was carried out to identify the rate-determining steps in the mechanism and to compare the importance of reactions I, IIa, IIb, and IIc on the concentration evolution of the major absorbing species. For each one, the sensitivity coefficient of reactions implying the studied species are presented versus time, $C_6H_5C(O)O_2$ (Figure 1a), O_3 (Figure 1b), $C_6H_5C(O)O_2H$ (Figure

TABLE 3: Reaction Scheme Used in the Simulation Calculation

	reaction	rate constant ^a	reference
Ι	$2C_6H_5C(O)O_2 \rightarrow 2C_6H_5C(O)O + O_2$	see text	this work
IIa	$C_6H_5C(O)O_2 + HO_2 \rightarrow C_6H_5C(O)O_2H + O_2$	see text	this work
IIb	$C_6H_5C(O)O_2 + HO_2 \rightarrow C_6H_5C(O)OH + O_3$	see text	this work
IIc	$C_6H_5C(O)O_2 + HO_2 \rightarrow C_6H_5C(O)O + OH + O_2$	see text	this work
III	$Cl + C_6H_5CHO \rightarrow C_6H_5CO + HCl$	9.60×10^{-11}	15
IV	$C_6H_5CO + O_2 + M \rightarrow C_6H_5C(O)O_2 + M$	5.71×10^{-12}	48
V	$CH_3OH + Cl \rightarrow CH_2OH + HCl$	5.50×10^{-11}	23
VI	$CH_2OH + O_2 + M \rightarrow HO_2 + CH_2O + M$	9.7×10^{-12}	52
VII	$C_6H_5C(0)O \rightarrow C_6H_5 + CO_2$	assumed instantaneous	
VIII	$OH + C_6H_5CHO \rightarrow C_6H_5CO + H_2O$	1.4×10^{-11}	12
IX	$C_6H_5 + O_2 + M \rightarrow C_6H_5O_2 + M$	$10^{-11} e^{(-1340/RT)}$	49
Х	$2C_6H_5O_2 \rightarrow 2C_6H_5O + O_2$	5.00×10^{-12}	16
XI	$C_6H_5O_2 + C_6H_5C(O)O_2 \rightarrow C_6H_5O + C_6H_5C(O)O + O_2$	1.00×10^{-11}	16
XII	$C_6H_5CO + Cl_2 \rightarrow C_6H_5COCl + Cl$	5.90×10^{-11}	16
XIII	$C_6H_5O + C_6H_5O_2 \rightarrow (C_6H_5)_2O + O_2$	5.00×10^{-12}	16
XIV	$C_6H_5O + C_6H_5O \rightarrow (C_6H_5)_2O_2$	1.49×10^{-11}	50
XV	$C_6H_5O + Cl_2 \rightarrow C_6H_5OCl + Cl$	1.00×10^{-14}	28
XVI	$C_6H_5O + C_6H_5C(O)O_2 \rightarrow (C_6H_5)_2C(O) + O3$	2.00×10^{-11}	16
XVII	$C_6H_5 + C_6H_5 \rightarrow C_{12}H_{10}$	$2.31 \times 10^{-11} e^{(-57/T)}$	51
XVIII	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.20 \times 10^{-13} e^{(600/T)}$	53
XIX	$HO_2 + Cl \rightarrow HCl + O_2$	$1.50 \times 10^{-11} e^{(222/T)}$	23
XX	$CH_3OH + OH \rightarrow CH_2OH + H_2O$	$2.42 \times 10^{-12} \mathrm{e}^{(-345/T)}$	52
XXI	$CH_2O + CI \rightarrow CHO + HCI$	$8.10 \times 10^{-11} e^{(-34/T)}$	23
XXII	$CHO + O_2 + M \rightarrow HO_2 + CO + M$	5.2×10^{-12}	52
XXIII	$CH_2OH + HO_2 \rightarrow CH_2O + H_2O_2$	2.00×10^{-11}	54
XXIV	$CH_2OH + Cl \rightarrow CH_2O + HCl$	6.64×10^{-10}	55

^{*a*} Units: $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ for bimolecular reactions and s^{-1} for unimolecular reactions.

1c), $C_6H_5O_2$ (Figure 1d). Depending on the studied species, some other key reactions are added for the sensitivity analysis.

The sensitivity analysis is based on the computation of the direct local first-order sensitivity coefficient for each species *i* in the reaction *j* at a reaction time *t*. The sensitivity coefficient is defined as follows, $(S_{ij})_t = (\delta \ln C_i)/(\delta \ln k_j)$. The perturbation generated on the rate constant of each reaction is around 10^{-3} .

Globally, reactions I, IIa, IIb, and IIc are the most sensitive reactions on the computed concentration of the main absorbing species. As can be expected, the consumption of the $C_6H_5C(O)O_2$ radical is sensitive to reactions I, IIa, IIb, and IIc (Figure 1a). As can be seen, the sensitivity of reaction IIa is more important mainly at the beginning of the reaction, and the sensitivity coefficients of reaction II at the beginning and the end of the reaction. The sensitivity coefficients of reactions XI and XVI (Table 3) show that radical-radical reactions are of minor importance in the determination of k_{II} .

As expected, for the concentration of ozone, at all times, reaction IIb is the most sensitive reaction, followed by reactions IIa, IIc, and I (Figure 1b).

The most sensitive reaction for the formation of C_6H_5C -(O)O₂H is IIa, whatever the reaction time. Other reactions do not favor the peracid production because they as well consume the benzoylperoxyl radical. As they are in concurrence with IIa, they present a negative sensitivity coefficient (Figure 1c).

Sensitivity analysis of $C_6H_5O_2$ was carried out because its contribution to the global OD signal is relatively important. As can be seen in Figure 1d, reactions producing $C_6H_5C(O)O$ present a positive sensitivity coefficient vis a vis the concentration profile of $C_6H_5O_2$ (reactions I and IIc). In fact, the phenylperoxyl, $C_6H_5O_2$, is mainly produced via the decarboxylation of the $C_6H_5C(O)O$ radical (reaction VII, Table 3), followed by reaction IX (Table 3). Sensitivity coefficients of reactions IIa and IIc are negative, relatively to $C_6H_5O_2$ concentration, because these processes are in concurrence with the reaction producing $C_6H_5C(O)O$.

3. Computational Calculations. A theoretical study of the radical-radical reaction of benzoylperoxy with hydroxylperoxy using the Gaussian 03 suite, revision B.05,³⁰ was performed at the B3LYP/6-311++G(2d,pd) level. This method tends to underestimate H-shift reaction barriers and provides unreliable thermochemical predictions.^{31,32} Therefore, all of the species considered in the mechanism were also treated with CBS-QB3, with relative energies being corrected for differences in the zeropoint vibrational energy scaled by 0.99.33 These calculations represent a good compromise between accuracy and computational cost regarding the good agreement with the experimental heat of formation of free radicals.³⁴ Using the procedure described in the literature,³⁵ we calculated the heat of formation in the gas phase for all species involved to solve the master equation for a part of the benzoylperoxy radical mechanism. Unimolecular rate constant k(E) was computed using RRKM theory,³⁶ with the required sums and densities of states being





Figure 2. Cross sections of benzoylperoxyl radical (\blacklozenge , this work; \Box , ref 16), acetylperoxyl (*, ref 56), and benzylperoxyl (\triangle , ref 22).

calculated with B3LYP/6-311++G(2d,pd) geometries and unscaled frequencies. More details about the implementation of the time-dependent ME/RRKM analysis in CHEMRATE³⁷ are available in a series of other publications.^{38–40} The accuracy of the method implemented in CHEMRATE was found to be adequate through extensive comparisons between experimental and theoretical data.^{41,42} We did not treat low-frequency internal rotations as hindered rotors, and our simulations included only the most stable conformer of each species. Collisional stabilization was treated using the exponential down model with the average energy transferred per collision ($\langle E_d \rangle$) assumed to be 300 cm⁻¹. The bath gas was taken to be Ar at 298 K with Leanard-Jones parameters of $\sigma = 4.4$ and $\varepsilon = 216$ K. These simplifications will affect numerical accuracy but should not detract from the validity of our conclusions.

IV. Results and Discussion

1. Cross Sections. *Results and Comparison*. Mean cross section values of $C_6H_5C(O)O_2$ (average of six determinations) between 220 and 280 nm, obtained from the curves of OD = f(t) are listed in Table 1 and plotted in Figure 2, where they are compared with values found in the literature.¹⁶

The UV absorption spectrum of $C_6H_5C(O)O_2$ consists of a broad continuum that decreases at upper wavelengths. As can be seen, this compound absorbs strongly relative to the other absorbing species. The comparison between the benzoylperoxy radical and both acetylperoxyl and benzylperoxyl radicals shows that the formers' UV absorption spectra are at least two times higher in intensity. It may be due to a conjugated effect of the aromatic ring and the acylperoxyl function.

Cross section values of $C_6H_5C(O)O_2$ determined in the present work are approximately half of those reported previously in ref 16 (Figure 2). This factor can be attributed to

• The large discrepancies in the benzaldehyde cross section values used to perform calculations. The experimental OD at origin OD(t = 0), determined by extrapolation, represents the OD attributed to the peroxyl radical diminished by the benzaldehyde consumption to form C₆H₅C(O)O₂, $\Delta C_{benzaldehyde}$:

$$OD(t = 0) = \sigma_{\text{RO2},\lambda} l \cdot [\text{RO}_2]_0 - \sigma_{\text{benzaldehyde},\lambda} \cdot l \cdot \Delta C_{\text{benzaldehyde}}$$
(4)

where l is the optical path.

As the consumed benzaldehyde is converted to benzoylperoxyl radical RO₂, $\Delta C_{\text{benzaldehyde}} = [\text{RO}_2]_0$, with $[\text{RO}_2]_0$ being the initial peroxy concentration. It turns out that the calculation of $\sigma_{\text{RO}_2\lambda}$ depends on the benzaldehyde cross sections $\sigma_{\text{benzaldehyde},\lambda}$

$$\sigma_{\text{RO2},\lambda} = \frac{\text{OD}(t=0) + \sigma_{\text{benzaldehyde},\lambda} \cdot l \cdot [\text{RO}_2]_0}{\cdot l \cdot [\text{RO}_2]_0}$$
(5)

Values of the benzaldehyde cross section used in this study are those recommended by ref 22. They are about 1.5 time smaller than those used in ref 16, explaining partially the discrepancies in the benzoylperoxyl cross sections.

• The experimental method. Our experiments were carried out by laser photolysis versus flash photolysis from ref 16. The post-flash dead time in laser photolysis (time between the laser pulse and the information recording) is about 10 μ s. This possibility to get information in the neighborhood of t = 0differentiates the laser photolysis technique from others and allows better extrapolation of the time origin, leading to higher confidence in cross section determinations. The post-flash dead time in the flash photolysis experiments of ref 16 was about 250 μ s. During this time, the consumption of the benzoylperoxyl radical and the formation of absorbing species are relatively important. This can affect the determination of the initial ODs. Therefore, the values of ref 16 may be overestimated.

Systematic Errors. The benzoylperoxy radical cross sections, σ_{λ} , were determined relative to the σ_{250} of the ethylperoxy radical and by extrapolating the signal to t = 0 to optimize initial ODs. The ethylperoxy radical cross section used is given in ref 24, with 5% relative uncertainty. The initial absorbance was optimized using the nonlinear least-squares fitting to fit the first points of the signal obtained just after the laser pulse.

As mentioned above, the determination of the benzoylperoxy radical is linked to the benzaldehyde cross section, which strongly rises up from 250 to 240 nm, inducing a source of error in its determination. As a result, below 245 nm, an uncertainty of 30% affects the cross section determination, whereas the estimated total error does not exceed 20% above 250 nm.

2. Data Simulation and Determination of Kinetic Parameters. Transient absorption profiles were recorded at wavelengths of 220, 245, 250, 255, and 260 nm following the pulsed photolysis of the (Cl₂/C₆H₅CHO/CH₃OH/O₂/N₂) mixture. First, $k_{\rm I}$ was extracted under experimental conditions where [CH₃OH] = 0. Then, to extract the kinetic parameters of reaction II with confidence, experiments were carried out at various concentrations of HO₂ and C₆H₅C(O)O₂ by varying the concentrations of benzaldehyde and methanol. Kinetic parameters were determined by analyzing the temporal profiles of OD obtained in the 250-255 nm spectral region where the benzoylperoxy radical absorption is important. At 250-255 nm, the absorptions of HO₂ and benzaldehyde are small relative to the absorption of $C_6H_5C(O)O_2$. As a consequence, HO_2 and benzaldehyde do not affect the absorption evolution of the benzoylperoxy radical. Experiments at 245 and 260 nm were used to validate the kinetic parameters determined in the spectral region of 250-255 nm.

Self-Reaction of $C_6H_5C(O)O_2$. The value of k_1 was determined at room temperature (293 K) and compared with a previous study to validate the experimental device. The mean of six experiments leads to $k_1 = (1.5 \pm 0.6) \times 10^{-11}$ cm³·molecule⁻¹·s⁻¹ at 293 K.

Caralp et al.¹⁶ have obtained the following Arrhenius expression of $k_{\rm I}$ between 298 and 460 K using a least-squares fitting.

 $k_{\rm I} = (3.1 \pm 1.4) \times 10^{-13} \exp(1110 \pm 160/T) \,{\rm cm}^3 \cdot {\rm molecule}^{-1} \cdot {\rm s}^{-1}$

giving $k_{\rm I} = (1.3 \pm 0.6) \times 10^{-11} \,{\rm cm^3 \cdot molecule^{-1} \cdot s^{-1}}$ at 293 K, which is in good accordance with our results.

This determination of $k_{\rm I}$ in the 250–255 nm spectral region depends mainly on the cross section values of RO₂ ($\sigma_{\rm RO2}$) and benzaldehyde ($\sigma_{\rm benzaldehyde}$). In our work, ($\sigma_{\rm RO2}$) and ($\sigma_{\rm benzaldehyde}$) values are, respectively, 1.5 and 2–3 times lower than those used in ref 16. In the calculation of the OD, the ($\sigma_{\rm RO2}$) discrepancy can be compensated for by those of $\sigma_{\rm benzaldehyde}$ and vice versa. Consequently, despite these large discrepancies in cross sections, the $k_{\rm I}$ value obtained in this work is close to that determined in ref 16.

Reaction between $C_6H_5CH_2O_2$ and HO_2 . Experiment Analyses. The kinetic simulation of the different signals, using the mechanistic scheme, allows the determination of the kinetic parameters of reaction II. For each temperature, experiments and thus simulations are conducted at different wavelengths and initial ratios [methanol]_0/[benzaldehyde]_0 to ensure the accuracy of the determined kinetic parameters.

Figure 3 compares the experimental signals recorded at three wavelengths under the same experimental conditions. Figures 4-6 detail the curves presented in Figure 3 by adding the individual simulated contributions to the OD of the absorbing species.

Figure 3 shows that the mechanistic scheme and the kinetic parameters match whatever the wavelength since experimental and simulated OD are consistent. In analyzing these curves, special attention must be given to the OD at the origin and the residual OD resulting from stable products' absorption.

• Initial OD results both from benzoylperoxyl formation and benzaldehyde consumption. Before starting the reaction, the initial OD is recorded with the initial concentration of benzaldehyde that is a high absorbing species (Table 2). When the reaction starts, the benzaldehyde concentration immediately decreases as benzoylperoxyl is formed; as a result, benzaldehyde has a negative contribution to the global OD. The lower initial OD at 260 nm is mainly due to the lower benzoylperoxyl cross section at this wavelength (Figures 3 and 5).

• As a consequence of the large absorbing coefficient of benzaldehyde at 245 nm (Table 2), the residual experimental OD (up to 0.001 s) is lower at 245 nm than at 250 and 260 nm (Figure 3). The residual OD (up to 0.001 s) is quite the same at 250 and 260 nm since the stable absorbing products of the reaction (O₃, C₆H₅C(O)O₂H, and C₆H₅C(O)OH in prevalent order in terms of OD) as well as benzaldehyde have cross sections of the same magnitude order (Table 2). Figures 4–6 indicate the high contribution of O₃ to the residual OD. Moreover, Figures 3 and 6 justify the choice of 250 nm as the wavelength where kinetic parameters are extracted, such as minor benzaldehyde interference and higher sensitivity to the benzoylperoxyl OD contribution.

• When the initial ratio [methanol]₀/[benzaldehyde]₀ is high, a real incidence of the OD signal decreasing can be seen. The OD decrease is faster at higher initial methanol concentration because it leads to a higher initial HO₂ concentration (Figure 7). The rate of RO₂ consumption increases.

• The rate of OD decreasing is lower at higher temperature (Figure 8). This is due to the fact that the consumption of RO₂ ($k_{\rm II}$ and $k_{\rm I}$) decreases when the temperature increases. Moreover, the residual OD increases when the temperature increases. This is due to the fact that $\beta_{\rm O3}$ increases with temperature (Table 4).

Kinetic Parameter Determination Using Simulation. The simulation fitting is achieved by varying the rate constant k_{II}



Figure 3. Influence of wavelength on the OD = f(t). Comparison model and experiment for T = 295 K, P = 80 Torr, $[Cl]_0 = 3.7 \times 10^{14}$ molecule·cm⁻³, [benzaldehyde]_0 = 9.5×10^{14} molecule·cm⁻³, r =[methanol]_0/[benzaldehyde]_0 = 4.



Figure 4. OD = f(t) of the strongest absorbing species: Comparison of model and experiment for $\lambda = 245$ nm, T = 295 K, P = 80 Torr, [Cl]₀ = 3.7 × 10¹⁴ molecule · cm⁻³, [benzaldehyde]₀ = 9.5 × 10¹⁴ molecule · cm⁻³, $r = [methanol]_0 [benzaldehyde]_0 = 4$.

and the branching ratios β_{O2} , β_{O3} , and β_{OH} independently for each experiment. The best simulation is chosen by eye. Thanks to the numerous experiments in different experimental conditions (reagent concentration, methanol/benzaldehyde ratio, laser energy) for each temperature, we manage to identify parameters with enough credibility.

At ambient temperature, we have found two independent results within the uncertainty ranges specified:

• $k_{\rm II} = 3.82 \pm 1.10 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ and $(\beta_{02};\beta_{03};\beta_{0H}) = (0.80 \pm 0.10; 0.20 \pm 0.05; 0).$

• k_{II} = 3.82 ± 1.10 × 10⁻¹¹ cm³•molecule⁻¹•s⁻¹ and ($\beta_{\text{O2}};\beta_{\text{O3}};\beta_{\text{OH}}$) = (0.65 ± 0.10;0.15 ± 0.10;0.2 ± 0.05).

As the latter result is in agreement with the semiquantitative determination of Dillon et al.,¹⁹ we validated the second solution. The theoretical study, presented later in the paper confirms the existence of path IIc. In this mechanistic scheme considering three paths, $k_{\rm II}$ and the branching ratio were converging toward the values reported in Table 4. As can be seen, $\beta_{\rm O3}$ increases with temperature, whereas $\beta_{\rm O2}$ decreases and $\beta_{\rm OH}$ remains constant (Table 4). The linear least-squares fitting of all of the



Figure 5. OD = f(t). Comparison of model and experiment for $\lambda = 260 \text{ nm}$, T = 295 K, P = 80 Torr, $[Cl]_0 = 3.7 \times 10^{14} \text{ molecule} \cdot \text{cm}^{-3}$, [benzaldehyde]_0 = $9.5 \times 10^{14} \text{ molecule} \cdot \text{cm}^{-3}$, $r = [\text{methanol}]_0/[\text{benzaldehyde}]_0 = 4$.



Figure 6. OD = f(t) of the strongest absorbing species. Comparison of model and experiment for $\lambda = 250$ nm, T = 295 K, P = 80 Torr, $[Cl]_0 = 3.7 \times 10^{14}$ molecule·cm⁻³, [benzaldehyde]_0 = 9.5 $\times 10^{14}$ molecule·cm⁻³, $r = [methanol]_0 [benzaldehyde]_0 = 4$.

rate constants provided by the experiments at different temperatures leads to the Arrhenius expressions

$$k_{\rm II}(T) =$$

(1.10 ± 0.20) × 10⁻¹¹ exp(364 ± 200/T) cm³·molecule⁻¹·s⁻¹

$$k_{\text{IIa}}(T) =$$

(4.80 ± 0.50) × 10⁻¹³ exp(1184 ± 300/T) cm³·molecule⁻¹·s⁻¹

$$k_{\text{IIb}}(T) = (5.20 \pm 0.50) \times 10^{-10} \times \exp(-1334 \pm 300/T) \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$$

10

$$k_{\text{IIc}}(T) =$$

(2.30 ± 0.20) × 10⁻¹² exp(364 ± 200/T) cm³·molecule⁻¹·s⁻

At room temperature, $k_{\rm II}$ is 3.82×10^{-11} cm³·molecule⁻¹·s⁻¹. The rate constant of the reaction between CH₃C(O)O₂ and HO₂ has been determined to be 1.42×10^{-11} cm³·molecule⁻¹·s⁻¹



Figure 7. Influence of the ratio $r = [methanol]_0/[benzaldehyde]_0$ on the OD = f(t). Comparison of model and experiment at 250 nm for r = 1, $[Cl]_0 = 2.2 \times 10^{14}$ molecule·cm⁻³, $[benzaldehyde]_0 = 1.0 \times 10^{15}$ molecule·cm⁻³, T = 295 K, P = 80 Torr and r = 4, $[Cl]_0 = 3.7 \times 10^{14}$ molecule·cm⁻³, $[benzaldehyde]_0 = 9.5 \times 10^{14}$ molecule·cm⁻³.



Figure 8. Influence of temperature on the OD = f(t). Comparison of model and experiment at $\lambda = 250$ nm for T = 295 K, P = 80.2 Torr, $[Cl]_0 = 3.7 \times 10^{14}$ molecule·cm⁻³, r = 4, $[C_6H_5CHO]_0 = 9.5 \times 10^{14}$ molecule·cm⁻³ and T = 337 K, P = 80.0 Torr, $[Cl]_0 = 3.7 \times 10^{14}$ molecule·cm⁻³, r = 4, $[C_6H_5CHO]_0 = 6.1 \times 10^{14}$ molecule·cm⁻³.

in one study⁴³ and 1.50×10^{-11} cm³·molecule⁻¹·s⁻¹ in an other.¹⁸ Thus, substituting the methyl group by a phenyl group enhances the rate constant by three times. The benzyl group has a rather large influence on the kinetic rate.

The value of the branching ratio is validated by the strong absorption of O_3 at 250 nm in comparison with other reaction products (Table 2). According to the mechanistic scheme (Table 3) there are two ways of production of O_3 , reactions IIb and XVI. Although reaction XVI is mentioned in the mechanism (Table 3) to complete the mechanistic scheme, its contribution to O_3 production is less than 0.1%. As discussed previously, this is confirmed by the sensitivity analysis where the sensitivity coefficient of reaction XVI toward O_3 is negligible relative to that of reaction IIb (Figure 1b).

As a consequence, O_3 can be totally assigned to the reaction IIb. Thus, β_{O3} determines the experimental signal residual absorption above 0.005 s. At room temperature, it is determined to be 0.15 \pm 0.10. For the reaction between CH₃C(O)O₂ and HO₂, the branching ratio β_{O3} is a little higher since it ranges between 0.20 and 0.33 at room temperature.^{43–45} It is either independent of temperature^{43,44} or increases with temperature.⁴⁵

TABLE 4: Rate Constant Values and Branching Ratio Obtained for the Reaction $C_6H_5C(O)O_2 + HO_2$ at Different Temperatures

temperature (K)	$k_{\rm II} ({\rm cm}^3 \cdot {\rm molecule}^{-1} \cdot {\rm s}^{-1})$	$eta_{ ext{O3}}{}^a$	$eta_{ ext{OH}}{}^a$	number of trials
295	$3.82 \pm 1.10 \times 10^{-11}$	0.15 ± 0.10 (0,24)	0.20 ± 0.05 (0,22)	12
316	$3.65 \pm 1.00 \times 10^{-11}$	0.20 ± 0.10 (0,24)	0.20 ± 0.05 (0,22)	8
337	$3.32 \pm 0.92 \times 10^{-11}$	0.30 ± 0.10 (0,24)	$0.20 \pm 0.05 \ (0,22)$	8
357	$3.10 \pm 0.85 \times 10^{-11}$	$0.40 \pm 0.10~(0,\!24)$	$0.20 \pm 0.05 \; (0,\!22)$	8

^a The branching ratio obtained from theoretical kinetic simulation is in italic in parentheses.

In our experiments, it increases significantly with temperature and reaches 50% at 357 K (Table 4).

The value of $\beta_{\rm OH} = 0.20 \pm 0.05$ is independent of temperature. This value is in agreement with the "semi-quantitative" value determined by Dillon et al.¹⁹ It is, however, lower than the branching ratio determined for the reaction CH₃C(O)O₂ +HO₂ ($\beta_{\rm OH} = 0.5 \pm 0.2^{19}$ or $\beta_{\rm OH} = 0.43 \pm 0.10^{20}$).

3. Systematic Errors. Uncertainties in the determination of the rate constant k_{II} , β_{O3} and β_{OH} are mainly due to to following:

(1) Cross sections values. The computed ODs take into account the absorption of the following species: $C_6H_5C(O)O_2$, H₂O₂, HO₂, C₆H₅CHO, C₆H₅, C₆H₅O₂, C₆H₅O, C₆H₅COCl, C₆H₅OCl, (C₆H₅)₂O, (C₆H₅)₂O₂, C₆H₅C(O)OH, and C₆H₅C- $(O)O_2H$. A sensitivity analysis shows that the cross section values of the H₂O₂, C₆H₅ C₆H₅COCl, C₆H₅OCl, (C₆H₅)₂O, and $(C_6H_5)_2O_2$ have negligible effect on the simulation results. A perturbation of 100% on these parameters implies a contribution of less than 2% to the total error of $k_{\rm II}$. One of the main sources of systematic errors on the global rate constant determination is the cross sections of some intermediate reactive species such as the phenylperoxyl radical $C_6H_5O_2$, the phenoxy radical C₆H₅O, and the hydroperoxyl radical HO₂. The cross sections of the phenoxy radical were determined at 18% in ref 27. The cross sections of C₆H₅O₂ were estimated in ref 28, leading to an error of 20%.

Moreover, among the species having an influence on the OD is benzaldehyde. As mentioned above when discussing $C_6H_5C(O)O_2$ cross sections, the benzaldehyde cross sections and thus their uncertainties have a great influence on the OD at the origin as well as on the residual OD level. Nevertheless, above 250 nm, errors linked to the benzaldehyde cross section should not exceed 10%.

The remaining species, O_3 , $C_6H_5C(O)OH$, and $C_6H_5C(O)O_2H$, are the main absorbing stable products. These compounds influence the residual absorption level at times above 0.001 s (Figures 4-6). O₃ cross section values are well-known with a confidence of 5%.46 C6H5C(O)OH cross sections have been experimentally determined for the study at about 20%. Unfortunately, cross section values of $C_6H_5C(O)O_2H$ are not available in the literature. Knowing that $CH_3C(O)O_2H$ cross sections are about 2.5 times higher than those of CH₃C(O)OH,²⁶ the same ratio has been applied to determine the cross sections of C₆H₅C(O)O₂H relative to those of C₆H₅C(O)OH. Uncertainties on $C_6H_5C(O)O_2H$ cross sections lead to an uncertainty on the branching ratio. A perturbation of 50% on the cross sections of C₆H₅C(O)O₂H implies a variation of 15, 30, and 15% on the branching ratios β_{O2} , β_{O3} , and β_{OH} , respectively. Nevertheless, the cross sections set by analogy fit the experimental results under all experimental conditions, implying that a good confidence can be associated with these values.

(2) Initial concentration and reagent stability. The simulation accuracy is related to the initial chlorine atoms concentration and the ratio benzaldehyde/methanol. In each experiment, the initial concentration of chlorine atoms $[Cl]_0$ was determined relative to the ethylperoxy radical concentration, $[Cl]_0 =$

 $[C_2H_5O_2]_0 = [C_6H_5C(O)O_2]_0 + [HO_2]_0$ (where $[HO_2]_0$ is equal to 0 when $[CH_3OH]_0/[C_6H_5CHO]_0 = 0$). This relation is valid if the initial molecular chlorine concentration is constant. This constancy depends mainly on the stability of the laser energy during the experiment. The initial chlorine and benzaldehyde concentrations and the laser energy were determined before and after each experiment. Perturbations were less than 5% for the initial concentration of benzaldehyde, and 1% for the laser energy. The ratio methanol/benzaldehyde was approximately constant at 10%.

(3) Reaction scheme used to reproduce our experiments and to extract the kinetic parameters. This model was established as described in the Experimental Section. Most of the kinetic data were taken from the experimental studies available in the literature (Table 3). Nevertheless, four reactions, namely, X, XI, XIII, and XIV (Table 3), involving C_6H_5O and $C_6H_5O_2$, were set by analogy to ref 16. Simulations show that the kinetic properties of the phenoxy and phenylperoxy radicals have no influence on simulation; varying the rate constant by a factor of 10 has no influence on the simulated curve. The sensitivity analysis confirms the negligible influence of these processes, as can be seen in Figure 1.

A comparison of the rate constants for reactions I and II shows that when HO_2 is present in the reaction mixture, RO_2 reacts preferentially with HO_2 . The sensitivity coefficients of reactions IIa–IIc are overall higher than those of reaction I



Figure 9. Different simulations within the uncertainty range of the rate constant and branching ratio for an experiment (\blacklozenge) at 250 nm for T = 295 K, P = 80 Torr, $[CI]_0 = 3.7 \times 10^{14}$ molecule·cm⁻³, [benzaldehyde]_0 = 9.5 $\times 10^{14}$ molecule·cm⁻³, $r = [methanol]_0/$ [benzaldehyde]_0 = 4. Mean fitting curve $k_{II} = 3.82 \times 10^{-11}$ cm³·molecule⁻¹·s⁻¹ ($\beta_{02};\beta_{03};\beta_{OH}$) = (0.65;0.15;0.20). (a) Effect of -30% variation of k_{II} . (b) Effect of +30% variation of k_{II} . (c) $k_{II} = 3.82 \times 10^{-11}$ cm³·molecule⁻¹·s⁻¹ ($\beta_{02};\beta_{03};\beta_{OH}$) = (0.55;0.20;0.25). (d) $k_{II} = 3.82 \times 10^{-11}$ cm³·molecule⁻¹·s⁻¹ ($\beta_{02};\beta_{03};\beta_{OH}$) = (0.65;0.05;0.30).

 TABLE 5:
 Thermodynamic Parameters

reaction	ΔE^a	$CBS-\Delta_r H$	$\text{CBS-}\Delta_{\mathrm{r}}G$	$CBS-\Delta_r S$	$\Delta_{\rm r} H^{\circ}_{298 \rm K}{}^{b}$
IIa	-37.22	-42.09	-40.09	-5.10	-41.79
IIb	-25.73	-36.93	-35.64	-4.33	-37.32
IIc	-11.24	-5.28	-14.47	30.82	-4.88

^{*a*} Energies B3LYP/6-311G++(2d,pd). ^{*b*} Using experimentally available values.

(Figure 1a). Nevertheless, the influence of $k_{\rm I}$ depends on the ratio of methanol/benzaldehyde. At high ratio, the influence of $k_{\rm I}$ is negligible; a perturbation of 40% on $k_{\rm I}$, corresponding to the uncertainty range, implies a variation of either 15% on $k_{\rm II}$ or a variation of 20% on either the phenoxy or the phenylperoxy cross sections. The variation of $k_{\rm II}$ remains within the domain of uncertainty since we have determined at ambient temperature that $k_{\rm II} = 3.82 \pm 35\%$ cm³·molecule⁻¹·s⁻¹. Moreover, the variation of cross sections is within the uncertainties range. At low ratio, the influence of $k_{\rm I}$ is much more important. A perturbation of 40% on $k_{\rm I}$, corresponding to the uncertainty range, implies a variation of 60% on $k_{\rm II}$. These values are not within the range of uncertainty. Therefore, experiments were conducted under various experimental conditions for a ratio r between 1 and 4 to validate the kinetic parameters of $k_{\rm II}$.

Finally, the uncertainties associated with the cross section values, the initial concentrations, the reagents' stability, and the reaction scheme used both for reproducing our experiments and extracting the kinetic parameters result in approximately a 30% error in the values of $k_{\rm II}$ and the uncertainties ranges on $\beta_{\rm O3}$ and $\beta_{\rm OH}$, as mentioned in Table 4. Figure 9 shows the variation of the fit with changes in the different kinetic parameters to

give a better idea of these uncertainties. As can be seen, uncertainties on the rate constant influence mainly the curving, while uncertainties on the branching ratio influence the residual OD.

4. Quantum Calculation Results. Different mechanisms and thermodynamic quantities computed for each species involved in the different reaction steps were tested. The results of this study concerning reaction II suggest a mechanism involving a radical-radical coupling between benzovlperoxy and hydroxylperoxy with the formation of a stable intermediates that may decompose, yielding the products of reactions IIa, IIb, and IIc. These three reaction pathways are in competition. However, the quantum calculation does not directly show whether or not the different reaction paths are competitive. Channels IIa and IIb are found to proceed via hydrogen atom transfer and seem to be the dominant exothermic pathways; CBS- $\Delta_r H$ are -42.09 and -36.93 kJ/mol for IIa and IIb, respectively (Table 5). The reaction IIc is also exothermic but seems to be of minor importance (Table 5), CBS- $\Delta_r H = -5.28$ kJ/mol. Thermodynamic data favor reactions IIa and IIb to reaction IIc.

A combination of master equation calculations and kinetic simulations were performed. They will be presented in detail in a related theoretical paper. Briefly, the goal of these calculations is to determine whether or not the experimentally observed yields can be reproduced within the uncertainties of the calculations. Direct simulation, without lowering barriers, shows that the chemically activated intermediates **A1** and **A2** (Figure 10) formed from benzoylperoxy and hydroxylperoxy radicals decompose back to the reactants. The remaining species once thermalized are as follows:



Figure 10. Structures of key species (intermediate complex) considered for kinetics simulations (determined by B3LYP/6-311++G(2d,pd), bond lengths in Angstroms).



Figure 11. Profile energy surface considered for kinetic simulation (determined by B3LYP/6-311++G(2d,pd)).

• The intermediate A1 via TS1 (Figures 10 and 11) forms a hydroxytetroxide $C_6H_5C(O)O_3H$ intermediate, which decomposes with ~24% yield via the TS3 path (reaction IIb) to form benzoic acid and O₃ and ~22% yield via TS4 path (reaction IIc) to form OH, O₂, and C₆H₅CO.

• The intermediate A2 may undergo hydrogen atom transfer from HO₂ via TS2 (Figures 10 and 11) to form a peracetic acid $C_6H_5C(O)O_2H$ with \sim 54% yield via path IIa.

The predicted branching ratio for IIa/IIb/IIc is therefore $(\beta_{02};\beta_{03};\beta_{0H}) \approx (0.54;0.24;0.22)$. To further investigate the

proposed mechanism, calculations were carried out to determine the temperature dependence of the product formed via this mechanism (Figure 11). The data are shown in Table 5. At ambient temperature, ME analysis gives $\beta_{OH} = 0.22$, in accordance with the experimental value. However, results from these calculations predict that the product yields are essentially independent of temperature over the range of 293–357 K. In fact, the theoretical kinetic simulation concerning β_{OH} and β_{O3} is highly sensitive to the energy of transition states **TS3** and **TS4**. In fact, a variation of 1–2% on the energy (0.03 kcal) of these transition states leads to 99% variation of either β_{OH} or β_{O3} . The branching ratio of path IIa is not sensitive to the variation (1–2 kcal) of energy of the intermediate species because the gap between intermediates **A1** and **A2** is significant. Therefore, regarding the high sensitivity of β_{OH} or β_{O3} relative to the energies of transition states, the temperature effect observed experimentally (less than 30% on β_{O3}) might not be observed using ME. Thus, the discrepancies between experimental observations and calculations may be a consequence of the uncertainties of both experimental determinations and theoretical calculations. Despite these discrepancies, the theoretical study supports the existence of complex intermediate states and justifies that path IIc is a possible path.

According to these results, the proposed mechanism appears to be consistent at ambient temperature with the 15% yield of ozone and 20% yield of OH observed experimentally.

V. Conclusion

This study gives a new accurate spectrum and the kinetic behavior of the benzoylperoxy radical using the pulsed laser photolysis technique. The UV spectrum of the radical has been determined in the spectral region of 220-280 nm. It consists of a broad continuum that decreases at upper wavelengths. The presence of the conjugated effect of the aromatic ring and the acylperoxyl function implies that the absorption of benzoylperoxy radical is more important than that of other similar peroxy radicals. The self-reaction of $C_6H_5C(O)O_2$ has been studied at room temperature. The rate constant obtained is in good agreement with other studies found in the literature.¹⁶ Concerning the reaction between $C_6H_5C(O)O_2$ and HO_2 , this work reports the first quantitative kinetic study of this reaction at different temperatures. Comparing this rate constant with those of other acylperoxy radicals, it can be concluded that the aromatic group has a rather large influence on the kinetic rate. In addition, branching ratios ($\beta_{02};\beta_{03}$) were extracted by analyzing and simulating the temporal profiles. Approximate Arrhenius expressions are proposed for these parameters. The calculations and theoretical kinetic simulations reported have been used to explain the yields of products observed from the reaction of HO₂ radicals with benzoylperoxy radicals. The mechanism obtained in the theoretical study confirms the existence of the three channels with branching ratio values that agree with the experimental results. Good agreement is found between the experimental and the theoretical study at ambient temperature. Discrepancies appear between these two approaches at higher temperature since the theoretical approach is temperature-independent.

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