fact that energy minimization with respect to the out-of-plane deformation angle has never been considered explicitly. Correcting this deficiency might well help to lower the purely rotational part of the barrier height since such out-of-plane deformations are much more likely for partially rotated intermediates than for either perpendicular or planar structures. In general it is certainly not surprising that the present treatment overestimates the barrier height, since much more is known about the two equilibrium structures than about the intermediate conformation corresponding to the energy maximum of the reaction path.

Finally, while it is extremely difficult to quantitatively fix the details of the reaction surface, it is much easier to obtain a good qualitative picture of the operative mechanism in the thermochemically induced transformation of the two C_4H_6 isomers discussed in this paper. Instead of a linear process involving simultaneous rotation of CH_2 groups and stretching of the C_1–C_4 bond R, the reaction apparently involves a stepwise mechanism in which R is first varied to some intermediate value (about 60% of the way from its equilibrium cyclobutene value to its *cis*-butadiene counterpart), at which point rotation of the methylene groups then takes place without further change of R; thereafter R continues its variation toward the equilibrium value of the product species. The fact that rotation takes place only at a particular R value (or over a very narrow range of R in this region) indicates that it is at this distance that one should calculate orbital and state correlation diagrams for comparison with the qualitative theory given by Woodward and Hoffmann and by Longuet-Higgins and Abrahamson. Especially since the mode of rotation preferred is actually dependent on the reaction path taken, it seems of interest to construct such diagrams for the preferred stepwise mechanism considered in the present work.

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Kinetics of the Gas-Phase Unimolecular Decomposition of the Benzoyl Radical[1a]

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Abstract: The formation of CO has been measured volumetrically in the gas-phase PhCHO–I_2–PhCIO–HI system over the temperature range 341–394°. The rate of formation is associated with the unimolecular decomposition of the benzoyl radical as the rate-determining step: $\mathrm{Ph\dot{C}O} \rightarrow \mathrm{Ph\cdot} + \mathrm{CO}$ (3). In the pressure range 24–460 Torr, reaction 3 appears to be in the pressure-dependent region. Despite appreciable scatter in the data (±50%), it is possible to obtain reasonable Arrhenius parameters for k_3. Assuming a collisional efficiency of 1.0, the application of both RRK and RRKM unimolecular reaction theories is shown to yield the same high-pressure Arrhenius parameters, $\log (k_3, \mathrm{sec}^{-1}) = (14.6 \pm 0.5) - (29.4 \pm 1.8)/\theta$, where $\theta = 2.303RT$ kcal/mol. After correction to 298°K, this activation energy (29.2 kcal/mol) is in good agreement with the heat of reaction ($\Delta H_{298} = 27.5$ kcal/mol) and a back activation energy for addition of a phenyl radical to carbon monoxide of 2.3 kcal/mol. Reducing the collisional efficiency to 0.1 has the effect of decreasing the Arrhenius activation energy to 28.6 kcal/mol and, hence, $E_{3(298)}$ and $E_{-3(298)}$ to 28.4 and 1.5 kcal/mol, respectively.

The unimolecular decomposition of the benzoyl radical to a phenyl radical and carbon monoxide has received little attention. The formation of carbon monoxide in small quantities has been observed when benzoyl radicals were generated from the reaction of benzoyl peroxide with benzaldehyde at 80°[2] and from the photolytic decomposition of azodibenzoyl, both neat at 100° and as a 1% benzene solution at 80°.[3] These systems are complex and no quantitative rate data could be obtained.

The formation of benzoyl radicals in the gas phase has been measured from the pyrolysis of benzophenone,[4] benzil,[5] benzoyl chloride,[6a] and benzoyl bromide.[6b] In each case, the PhCO–R bond scission is much slower than the decomposition of the benzoyl radical and rates cannot be obtained for the secondary process.

The analogous unimolecular decompositions of the formyl and acetyl radicals have been much more extensively studied.[7] These reactions were in the pressure-

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(2) F. R. Rust, F. H. Seubold, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 70, 3258 (1948).

(3) D. Mackay, U. F. Marx, and W. A. Waters, *J. Chem. Soc.*, 4793 (1964).

(4) D. Clark and H. O. Pritchard, *ibid.*, 2136 (1956).

(5) E. Jacquiss, Ph.D. Thesis, University of Manchester, 1953.

(6) (a) M. Szwarc and J. W. Taylor, *J. Chem. Phys.*, 22, 270 (1954); (b) M. Ladaki, C. H. Leigh, and M. Szwarc, *Proc. Roy. Soc.*, *Ser. A*, 214, 273 (1952).

(7) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas-Phase Unimolecular Reactions," NSRDS-NBS 21, U. S. Department of Commerce, Washington, D. C., 1970.

Table I. Kinetic Data for the System Initiated from PhCHO, I_2, and HI

Temp, °C	[PhCHO]$_0$, Torr	[I_2]$_0$, Torr	[HI]$_0$, Torr	[PhCHO]$_m$, Torr	[I_2]$_m$, Torr	[HI]$_m$, Torr	[PhCIO]$_m$, Torr	[CO], Torr	Δp, Torr	Time, sec	$10^{-4}k_3$, sec^{-1}
340.9	18.5	29.0	15.3	13.2	26.6	17.5	1.8	7.0	7.1	1000	1.7
340.9	50.1	8.9	400.0	48.4	11.2	398.4	0.1	3.2	2.6	2100	3.0
342.7	17.3	8.1	30.2	12.6	8.1	30.7	0.3	8.7	8.7	3600	1.7
342.7	13.0	0.2	40.3	11.5	0.2	40.3	0.01	3.0	2.9	6000	2.8
342.7	24.8	0.5	120.2	22.9	1.4	118.5	0.02	3.8	3.3	4300	2.9
342.7	29.8	10.5	12.4	23.6	8.2	14.7	1.2	10.1	9.9	1000	1.9
357.3	31.1	0.9	126.5	20.5	2.1	124.2	0.03	21.1	20.4	9120	3.8
357.8	21.7	0.5	25.2	16.2	0.3	25.3	0.02	11.0	10.8	5600	1.8
394.5	10.6	2.9	18.7	5.3	2.1	19.4	0.07	10.4	10.5	700	3.3
394.4	9.9	0.9	32.8	6.4	0.9	32.8	0.02	7.0	6.8	750	4.3

Table II. Kinetic Data for the System Initiated from PhCHO and I_2

Temp, °C	[PhCHO]$_0$, Torr	[I_2]$_0$, Torr	[PhCHO]$_m$, Torr	[I_2]$_m$, Torr	[HI]$_m$, Torr	[PhCIO]$_m$, Torr	[CO], Torr	Time, sec	$10^{-4}k_3$, sec^{-1}
311.2	12.0	25.5	8.2	21.7	3.8	3.6	0.4	250	0.70
336.5	8.2	15.4	5.5	12.7	2.7	2.3	0.8	300	0.39
336.5	3.2	25.7	1.4	23.9	1.8	1.6	0.4	200	0.55
336.6	13.1	22.9	8.7	18.5	4.4	3.3	2.2	400	0.74
336.2	11.2	20.0	7.6	16.4	3.6	3.1	1.0	200	0.71
336.2	24.8	33.5	17.9	26.6	6.9	6.0	2.0	200	0.86
359.4	13.7	29.0	8.2	23.5	5.5	3.4	4.4	230	1.12
359.4	5.2	45.6	1.8	42.2	3.4	2.3	2.2	250	1.03
359.5	12.6	23.8	7.9	19.1	4.7	3.1	3.3	150	1.25
359.4	11.1	24.2	6.8	19.9	4.3	3.1	2.3	100	1.32
359.3	20.1	52.7	11.8	44.3	8.4	6.1	4.6	150	1.37

dependent region, and agreement between kinetics and thermodynamics is poor. Measured values of the activation energy for decomposition of the formyl radical average 14.2 kcal/mol, whereas the theoretical value calculated from the thermodynamics is 18.0 kcal/mol plus the activation energy for adding a hydrogen atom to carbon monoxide. The activation energy has been measured for both the unimolecular decomposition of the acetyl radical and the reverse reaction. Within ±2 kcal/mol, the thermodynamics are in agreement with the kinetics. However, the Arrhenius *A* factor for the unimolecular decomposition of $10^{10.3}$ sec^{-1} is in serious disagreement with transition-state theory.

During a study of the reactions of benzaldehyde with iodine,[7] formation of carbon monoxide was observed above 300°. This is formed at a convenient rate for measurement in a static system over the temperature range 300–400°. In this paper we present the kinetic studies of the decomposition of the benzoyl radical. Compared to the formyl and acetyl radicals, the Ph–Co bond is much stronger and there are more oscillators, so the decomposition should be only slightly in the pressure-dependent region.

Experimental Section

Materials. Benzaldehyde (Mallinckrodt) was degassed and distilled on the vacuum line. The gas chromatographically pure middle fraction was stored under vacuum and used for kinetic runs. Mallinckrodt I_2 was degassed at −10° and sublimed into a storage vessel attached to the heated inlet manifold. Matheson anhydrous HI was fractionated under vacuum and degassed at liquid nitrogen temperatures.

Apparatus. The reaction was measured in a static system using a cylindrical quartz reaction vessel thermostated with air inside a heated aluminum block. For reaction temperatures below 360°, the vessel was conditioned by deposition of a coating of Teflon from the di-*tert*-butyl peroxide initiated polymerization of 110 Torr of C_2F_4 at 190°. Above 360° this coating is unstable, and a coating deposited from the pyrolysis of 100 Torr of pentene at 430° for 24 hr was used to deactivate any reactive surface sites.

The reaction was monitored by three methods. The absorption of the reacting species was measured *in situ* using a Cary 15 spectrometer, as described previously.[8] The pressure was measured with a Pace differential transducer, CO_2 being used as a buffer between the metal diaphragm and the reaction gases. At the completion of a run, the reaction mixture was condensed in a liquid nitrogen cooled trap and the noncondensable gases were transferred to a gas buret with a mercury Toepler pump.

Procedure. The inlet manifolds and reaction vessel were evacuated to less than 10^{-4} Torr prior to a run. For some of the runs shown in Table I, I_2 was first added to the reaction vessel, followed by HI and then PhCHO. For higher pressures of HI, PhCHO was the first component added to the reaction vessel. The reaction was then initiated by the addition of a mixture of HI and I_2, previously mixed in the inlet manifold. HI was not added to a mixture of PhCHO and I_2. The presence of HI minimizes the concentration product [PhCHO][PhCIO] and hence the condensation of PhCHO with PhCIO.[9] The concentration of I_2 was calculated directly from the absorbance in the 450–500-nm region, where it is the only absorbing species.

The pressure of the reaction mixture for the runs in Table I was measured by nulling both sides of the differential pressure transducer with CO_2 to the anticipated reaction pressure. The reaction vessel was momentarily opened to one side of the transducer, and any small difference between the actual and estimated pressure was measured on an oil manometer. The precision of the measuring system was better than 0.1 Torr. However, the error in the sharing ratio of the reaction vessel to the transducer manifold is approximately 10%, so that the overall accuracy is decreased by deviation in the estimated to the actual reaction pressure. The pressure was monitored continuously from the start of the reaction for the shorter reaction times of the runs in Table II. In this time, diffusion between the reaction vessel and the connecting capillary tubes of the transducer is minimal.

The reaction mixture was condensed in a liquid nitrogen cooled trap at the completion of a run. Noncondensable gases were transferred to a gas buret and the volume and pressure were measured.

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[8] R. Walsh, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **87**, 4053 (1965).

[9] R. K. Solly and S. W. Benson, *ibid.*, **93**, 1592 (1971).

This pressure was converted into the equivalent pressure in the known volume of the reaction vessel at the reaction temperature. The noncondensable gases were analyzed by gas chromatography using a column packed with molecular sieve and a thermal conductivity detector. The retention time of the single peak was the same as that of an authentic sample of carbon monoxide.

HI and any CO_2 from the pressure transducer buffer was removed from the residue in the liquid nitrogen cooled trap by replacing the liquid nitrogen with a chloroform–liquid nitrogen slush bath. A liquid fraction at room temperature was distilled from the residue cooled in a salt–ice bath into a liquid nitrogen cooled cold finger. The distillate was analyzed as a liquid injection on a F and M Model 810 gas chromatograph using a silicone oil column and a flame ionization detector. The major product peak had the same retention time as benzene for the runs in Table I. Phenyl iodide and toluene were minor products, with PhCIO being detected for relatively high I_2/HI ratios. Phenyl iodide was the major condensation product detected by gas chromatography of the runs in Table II. Benzene, toluene, and PhCIO appeared as minor peaks. The latter because of poor sampling, owing to its low volatility, could not be analyzed reproducibly. No attempt was made to analyze the salt–ice bath residue, owing to the difficulty of separating the I_2.

Results and Discussion

Above 300°, PhCHO and I_2 react rapidly to form an equilibrium mixture with HI and PhCIO.[9]

$$\mathrm{PhCHO} + \mathrm{I_2} \rightleftarrows \mathrm{PhCIO} + \mathrm{HI} \qquad K_{12}$$

This equilibrium is established by way of a free-radical mechanism.

$$\mathrm{I_2} \rightleftarrows 2\mathrm{I}\cdot \qquad K_{\mathrm{I_2}}$$

$$\mathrm{PhCHO} + \mathrm{I}\cdot \rightleftarrows \mathrm{Ph\dot{C}O} + \mathrm{HI} \tag{1}$$

$$\mathrm{PhCO} + \mathrm{I_2} \rightleftarrows \mathrm{PhCIO} + \mathrm{I}\cdot \tag{2}$$

At these temperatures the benzoyl radical is unstable to unimolecular decomposition, but this reaction is relatively slow compared to the competing reactions −1 and 2.

$$\mathrm{PhCO} \longrightarrow \mathrm{Ph}\cdot + \mathrm{CO} \tag{3}$$

$$\mathrm{Ph}\cdot + \mathrm{I_2} \rightleftarrows \mathrm{PhI} + \mathrm{I}\cdot \tag{4}$$

$$\mathrm{Ph}\cdot + \mathrm{HI} \rightleftarrows \mathrm{PhH} + \mathrm{I}\cdot \tag{5}$$

Owing to the high Ph–R bond strength,[10] reactions 4 and 5 are irreversible for our experimental conditions. The steady-state concentration of PhĊO radicals may be calculated from reactions 1 and 2 by assuming that reaction 3 is a negligible perturbation.

$$[\mathrm{Ph\dot{C}O}] = \frac{[\mathrm{I}\cdot](k_1[\mathrm{PhCHO}] + k_{-2}[\mathrm{PhCIO}])}{(k_{-1}[\mathrm{HI}] + k_2[\mathrm{I_2}])} \tag{I}$$

where $[\mathrm{I}\cdot] = K_{\mathrm{I_2}}{}^{1/2}[\mathrm{I_2}]^{1/2}$. The rate of formation of CO is given by

$$\mathrm{d}[\mathrm{CO}]/\mathrm{d}t = k_3[\mathrm{Ph\dot{C}O}] \tag{II}$$

The ratio k_4/k_5 is approximately 5,[10] so the ratio [PhI]/[PhH] is determined by the relative concentration of I_2 to HI. With reference to the system after establishment of the rapid equilibrium K_{12}, the reaction stoichiometry is given by

$$\mathrm{PhCHO} \longrightarrow \mathrm{PhH} + \mathrm{CO}$$

for $[\mathrm{HI}] \gg [\mathrm{I_2}]$ and by

$$\mathrm{PhCHO} + \mathrm{I_2} \longrightarrow \mathrm{PhI} + \mathrm{HI} + \mathrm{CO}$$

for $[\mathrm{I_2}] > [\mathrm{HI}]$. For the runs shown in Table I, the ratio $[\mathrm{HI}]/[\mathrm{I_2}]$ is not sufficiently large that the formation of PhI may be neglected. However, we have a direct determination of I_2 at all stages of the reaction and of CO at the end of the reaction. The initial concentrations of PhCHO, HI, and I_2 were those added to the reaction vessel. Mean equilibrium concentrations of PhCHO, I_2, PhCIO, and HI were used in calculating k_3 from eq I and II. Initial equilibrium concentrations were calculated directly from the added reagents and K_{12}. Final equilibrium concentrations were calculated from $[\mathrm{PhCHO}]_f = [\mathrm{PhCHO}]_0 - [\mathrm{PhCIO}]_f - [\mathrm{CO}]$ and $[\mathrm{HI}]_f = [\mathrm{HI}]_0 + (-\Delta[\mathrm{I_2}]_f)$, where $[\mathrm{I_2}]_f$ was measured directly and $[\mathrm{PhCIO}]_f$ was calculated from K_{12}.

The situation is simplified for the runs in Table II, as the formation of PhH may be neglected compared to PhI. Mean equilibrium concentrations were calculated directly from the concentration of $[\mathrm{PhCHO}]_0$ and $[\mathrm{I_2}]_0$ added to the reaction vessel, and K_{12} is found with the relations $[\mathrm{PhCHO}]_m = [\mathrm{PhCHO}]_0 - [\mathrm{PhCIO}]_m - [\mathrm{CO}]/2$; $[\mathrm{I_2}]_m = [\mathrm{I_2}]_0 - [\mathrm{PhCIO}]_m - [\mathrm{CO}]/2$ and $[\mathrm{HI}]_m = [\mathrm{PhCIO}]_m + [\mathrm{CO}]/2$.

$k_1 = 10^{10.1-16.7/\theta}$ M^{-1} sec^{-1} and $K_{12} = e^{0.9-3500/RT}$ have been determined previously.[9,11] $k_{-1} = 10^{9.0-1/\theta}$ M^{-1} sec^{-1} and $k_2 = 10^{9.0}$ M^{-1} sec^{-1} may be estimated from analogous systems.[12] From these data, k_{-2} is calculated to be $10^{10.4-12.7/\theta}$ M^{-1} sec^{-1}. $K_{\mathrm{I_2}}{}^{1/2}$ calculated from JANAF tables[13] over the temperature range of interest is $10^{4.14-3.98/T}$ Torr$^{1/2}$. These values were substituted in eq I to obtain the mean steady-state concentration of PhĊO radicals. k_3 was calculated from eq II by fixing $\mathrm{d}[\mathrm{CO}]/\mathrm{d}t = [\mathrm{CO}]/(\text{reaction time})$.

As may be seen from Tables I and II, the variation of k_3 was ±50% as the $[\mathrm{PhCHO}]/[\mathrm{I_2}]$ ratio varied by 100-fold. However, the precision is not sufficient to obtain Arrhenius parameters directly from the experimental rate constants. Furthermore, the unimolecular decomposition, although only slightly so, is probably in the pressure-dependent region. We have calculated the Arrhenius A factor by assigning frequencies to the benzoyl radical and to the decomposition complex (Table III). The frequencies of the benzoyl radical

Table III. Molecular Parameters for PhĊO

	Radical	Complex
Frequencies, cm^{-1}, and degeneracy	3060 (5)	3060 (5)
	1700 (1)	1950 (1)
	1600 (3)	1600 (3)
	1483 (1)	1483 (1)
	1260 (3)	1290 (2)
	1160 (2)	1160 (2)
	1035 (3)	1035 (3)
	940 (3)	940 (3)
	785 (3)	785 (3)
	655 (2)	695 (1)
	440 (3)	440 (3)
	350 (2)	310 (1)
	154 (1)	175 (2)
	80 (1)	80 (1)
$I_AI_BI_C$, (gm cm^2)^3 × 10^{-113}	5.83	11.7
I_{ir}, (gm cm^2) × 10^{-40}		30.0[a]

[a] With a symmetry (≡ "foldness") of the barrier = 3.

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(10) A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **89**, 4578 (1967).

(11) R. K. Solly and S. W. Benson, *J. Chem. Thermodyn.*, in press.

(12) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 279 (1969).

(13) D. R. Stull, Ed., "JANAF Thermochemical Tables," The Dow Chemical Co., Midland Mich., 1963.

were assigned with reference to frequencies reported for benzoyl halides[14] and ethyl benzene.[15] The internal rotation of the CO group was considered as a vibration, with a frequency such that the entropy at 600°K was the same as that for a hindered internal rotor with a 3-kcal/mol barrier.[16]

Six frequencies were modified in forming the transition complex from the reactant radical. The Ph–CO stretch was taken as the reaction coordinate. The barrier to internal rotation of the CO group was reduced to zero, thus becoming a free internal rotation. Three vibrations associated with the relative skeletal bending of the phenyl and CO groups were reduced to 50% of their value in the radical. All previous radical decompositions have been found to fit this model.[17] The C=O stretching vibration was increased to the mean of that for a C=O and a C≡O stretch. In calculating the product of the moments of inertia for the complex, the Ph—CO bond length was increased from 1.52 to 2.52 Å, and the C=O bond decreased from 1.20 to 1.15 Å. The Arrhenius A factor was calculated from the partition functions for external rotation, vibration, and internal rotation. Symmetry corrections were included in the rotational partition functions. From the molecular parameters given in Table III, the A factor was calculated to be $10^{14.6}$ sec^{-1}.

Theoretical rate constants were calculated using both the quantum-statistical RRKM theory[18] and the classical RRK theory.[19] For the RRKM theory, the Arrhenius A factor is defined by the molecular parameters, while the critical energy is considered an adjustable parameter to obtain the best fit between experimental and theoretical rate constants. Vibrational energy levels at low energies of the complex were obtained by a direct count.[20] Energy sums and densities at higher energies were obtained from the Haarhoff approximation,[21] as modified by Whitten and Rabinovitch.[22,23]

RRK theoretical rate constants were calculated using the appropriate Gaussian quadrature formula for the Kassel integral, as described by Emanuel.[24] In order to compare the two theoretical methods, identical parameters were used for both calculations. The Arrhenius A factor was obtained as described previously. The activation energy (E_a) was calculated from the critical energy (E_c) by

$$E_c = E_a - \langle E^* \rangle - \langle E^\dagger \rangle - {}^1\!/_2(r^\dagger - r^* + 2)RT \quad \text{(III)}$$

where $\langle E \rangle$ is the mean vibration energy in excess of the ground-state energies and r the number of active rotations for the activated molecule (designated by an asterisk) and complex (designated by a dagger). The number of effective oscillators (s) was not considered as an adjustable parameter, but defined by

$$s = \frac{\langle E^* \rangle_{T_2} - \langle E^* \rangle_{T_1}}{(T_2 - T_1)R} \quad \text{(IV)}$$

where $(T_2 - T_1)$ is a small temperature difference at the approximate experimental temperature.

We must, in addition, estimate for $\mathrm{Ph\dot{C}O}$ its collision diameter and collisional efficiency. The steady-state concentration of $\mathrm{Ph\dot{C}O}$ radicals is approximately 10^{-7} Torr, so in all cases collision is with "inert" molecules of I_2 and HI. The term "inert" is only in relation to reaction 3, as reactions −1 and 2 are examples of reactive collisions. There are no directly analogous examples in the literature, but with reference to the recent paper by Spicer and Rabinovitch,[25] and references therein, we have assigned a collision diameter of 6 Å and chosen limits for the collisional efficiency of 1.0 and 0.1, the latter being equivalent to a reduction of the pressure to 10% of the original value for a collisional efficiency of 1.0.

These results are shown in Table IV for both RRKM and RRK calculations, excellent agreement being obtained between the two methods. Using a collisional efficiency of 1.0, the best fit to the experimental rate constants was obtained with Arrhenius parameters of

$$\log (k_3, \text{sec}^{-1}) = (14.6 \pm 0.5) - (29.4 \pm 1.8)/\theta$$

where $\theta = 2.303RT$ kcal/mol. The error in the A factor is that estimated from assigning the molecular frequencies, whereas that in E_a is derived from the error in the A factor combined with the scatter in the calculated E_a for each rate constant as listed in Table IV. It may be noted that the effect of a collisional efficiency of 0.1 is to reduce the activation energy to 28.6 kcal/mol. In the following discussion, we show first the parameters which are derived from a collisional efficiency of 1.0 immediately followed in parentheses by those derived from a collision efficiency of 0.1.

From $\Delta H_f{}^\circ{}_{298}(\mathrm{Ph\dot{C}O})$ = 26.1 kcal/mol,[9] $\Delta H_f{}^\circ{}_{298}(\mathrm{Ph\cdot})$ = 78.5 kcal/mol[26] and $\Delta H_f{}^\circ{}_{298}(\mathrm{CO})$ = −26.4 kcal/mol,[26] ΔH_{298} for reaction 3 is 26.0 kcal/mol. Correcting E_a to 298°K by eq III, $E_3(298°)$ = 29.2 (28.4) kcal/mol and E_{-3} (298°) = 3.8 (3.0) kcal/mol. This activation energy for the addition of a phenyl radical to CO is in reasonable agreement with activation energies of 3.9 and 5 kcal/mol reported for the addition of a methyl and ethyl radical, respectively.[27] The activation energy for radical addition may be correlated with the bond strength of the forming R–CO bond, this being 26.0, 13.0, and 10 kcal/mol for R = Ph, Me, and Et, respectively. The increased steric size of the phenyl radical does not seem to decrease the activation energy, although this may be compensated by the strong $\mathrm{Ph\text{–}\dot{C}O}$ bond.

As discussed in a previous paper,[9] the formation of toluene became more prominent with increasing reaction time and an increase in the surface-to-volume ratio

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[14] P. Delome, V. Lorenzelli, and A. Alemagna, *J. Chim. Phys Physicochim. Biol.*, **62**, 3 (1965).

[15] W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **37**, 95 (1946).

[16] P. J. Krusic and T. A. Rettig, *J. Amer. Chem. Soc.*, **92**, 722 (1970).

[17] C. W. Larson, B. S. Rabinovitch, and D. C. Tardy, *J. Chem. Phys.*, **47**, 4570 (1967); M. J. Pearson and B. S. Rabinovitch, *ibid.*, **42**, 1624 (1965); W. E. Falconer, B. S. Rabinovitch, and R. J. Cvetanović, *ibid.*, **39**, 40 (1963).

[18] R. A. Marcus, *ibid.*, **20**, 359 (1952).

[19] L. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, N. Y., 1932.

[20] B. S. Rabinovitch, R. F. Kubin, and R. E. Harrington, *J. Chem. Phys.*, **38**, 405 (1963).

[21] P. S. Haarhoff, *Mol. Phys.*, **6**, 337 (1963); **7**, 101 (1963).

[22] G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 2466 (1963).

[23] We are grateful to Professor Rabinovitch for a listing of this program.

[24] G. Emanuel, "Table of the Kassel Integral," Aerospace Corp. (TR-0200(4240-20)-5), El Segundo, Calif., 1969.

[25] L. D. Spicer and B. S. Rabinovitch, *J. Phys. Chem.*, **74**, 2445 (1970).

[26] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

[27] J. A. Kerr and A. C. Lloyd, *Trans. Faraday Soc.*, **63**, 2480 (1967).

Table IV. Experimental and Theoretical Rate Constants for Reaction 3

$10^3/T$, °K	Temp, °K	Pressure, Torr	$10^{-4}\ k_{\text{exp}}$, sec^{-1}	$k_{\text{uni}}/k_{\infty}{}^a$ RRKM[d]	$k_{\text{uni}}/k_{\infty}{}^a$ RRK[e]	$k_{\text{uni}}/k_{\infty}{}^b$ RRKM[f]	$k_{\text{uni}}/k_{\infty}{}^b$ RRK[g]	$10^{-4}\ k_{\infty}$,[a] sec^{-1}	E_a,[a,c] kcal/mol	$10^{-4}\ k_{\infty}$,[b] sec^{-1}	E_a,[b,c] kcal/mol
1.712	584.3	38	0.70	0.76	0.72	0.41	0.39	0.92	28.4	1.71	27.7
1.643	609.6	24	0.39	0.62	0.61	0.27	0.30	0.64	30.1	1.46	29.1
	609.6	29	0.55	0.65	0.63	0.32	0.32	0.85	29.8	1.73	28.9
	609.7	36	0.74	0.70	0.66	0.34	0.34	1.05	29.5	2.16	28.6
	609.3	31	0.71	0.67	9.64	0.33	0.32	1.06	29.5	2.15	28.6
	609.3	58	0.87	0.75	0.71	0.44	0.38	1.15	29.4	1.97	28.7
1.630	614.0	65	1.68	0.77	0.72	0.42	0.39	2.18	28.8	4.00	28.1
	614.0	462	3.00	0.93	0.90	0.71	0.65	3.23	28.4	4.23	28.0
1.623	615.8	60	1.68	0.76	0.71	0.42	0.38	2.20	28.9	4.00	28.2
	615.8	55	2.82	0.75	0.70	0.41	0.37	3.76	28.3	6.88	27.5
	615.8	150	2.86	0.86	0.80	0.57	0.50	3.32	28.4	5.01	27.9
	615.8	58	1.85	0.76	0.70	0.42	0.37	2.44	28.8	4.41	28.1
1.585	630.4	168	3.75	0.85	0.76	0.54	0.48	4.42	28.7	6.95	28.2
	630.9	53	1.82	0.72	0.62	0.37	0.32	2.53	29.4	4.92	28.6
1.582	632.5	43	1.12	0.68	0.64	0.35	0.30	1.65	30.1	3.20	29.2
	632.6	51	1.03	0.72	0.62	0.37	0.32	1.43	30.2	2.78	29.4
	632.5	36	1.25	0.67	0.61	0.30	0.29	1.87	29.9	4.17	28.9
	632.5	35	1.32	0.66	0.61	0.29	0.29	2.00	29.8	4.55	28.8
	632.4	73	1.37	0.75	0.66	0.40	0.36	1.83	29.9	3.43	29.1
1.500	667.6	38	3.32	0.59	0.54	0.30	0.23	5.64	30.1	11.10	29.2
	667.5	47	4.35	0.61	0.57	0.30	0.25	7.13	29.8	14.50	28.8

[a] Collisional efficiency = 1.0. [b] Collisional efficiency = 0.1. [c] Calculated from $k_{\infty} = 10^{14.6-E_a/\theta}$ sec^{-1}. [d] $k_{\infty} = 10^{14.6-29.4/\theta}$ sec^{-1}; E_c = 28.4 kcal/mol. [e] $k_{\infty} = 10^{14.6-29.4/\theta}$ sec^{-1}, s = 20. [f] $k_{\infty} = 10^{14.6-28.6/\theta}$ sec^{-1}; E_c = 27.6 kcal/mol. [g] $k_{\infty} = 10^{14.6-26.6/\theta}$ sec^{-1}; s = 20.

of the reaction vessel. A possible mechanism is *via* the condensation of PhCHO with PhCIO as reported by Staudinger and Anthes.[28]

$$\text{PhCHO} + \text{PhCIO} \rightleftharpoons \text{PhCHIOCOPh} \qquad (6)$$

The ester will react with HI to yield PhCHI_2,[29] and subsequent iodine atom catalyzed reactions in the presence of HI will yield PhCH_3.

$$\text{PhCHIOCOPh} + \text{HI} \rightleftharpoons \text{PhCHI}_2 + \text{PhCOOH} \qquad (7)$$

$$\text{PhCHI}_2 + 2\text{HI} \rightleftharpoons \text{PhCH}_3 + 2\text{I}_2 \qquad (8)$$

Reactions 6–8 have not been included in the kinetic calculations described in this paper. In the time of all runs in Tables I and II, PhCH_3 was a minor product compared to PhH or PhI. The rate of reaction 3 was calculated from the direct measurement of the volume of CO. The effect of reactions 6–8 would be to reduce the actual concentrations of PhCHO and HI according to the stoichiometric equation

$$2\text{PhCHO} + 2\text{HI} \longrightarrow \text{PhCH}_3 + \text{PhCOOH} + \text{I}_2$$

From eq I, the $\text{Ph}\dot{\text{C}}\text{O}$ steady-state concentration is proportional to [PhCHO], but inversely proportional to [HI], so a reduction in both concentrations is partly self-compensating. The formation of a small amount of PhCH_3 does not cause any significant error in the calculations of k_3.

Conclusion

Kinetic parameters for the unimolecular decomposition of the benzoyl radical are shown to be in good agreement with thermochemical data and transition-state models. Defining the Kassel s as a fixed parameter from the vibrational heat capacity, good agreement was obtained between classical RRK theory and quantum-statistical RRKM theory. This agreement of RRK and RRKM theory has been found to be general for all thermal reactions compared in this laboratory, including four-center eliminations from hydrazines and radical fragmentation of hydrazines and benzylamines.[30]

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(28) H. Staudinger and E. Anthes, *Chem. Ber.*, **46**, 1417 (1913).

(29) R. K. Solly and S. W. Benson, *J. Phys. Chem.*, **74**, 4071 (1970).

(30) R. K. Solly, D. M. Golden, and S. W. Benson, *ibid.*, in press.