Kinetics of the Gas-Phase Reaction of Benzaldehyde with Iodine. The Heat of Formation and Stabilization Energy of the Benzoyl Radical[1a,b]

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Abstract: The gas-phase reaction $PhCHO + I_2 \rightarrow PhCIO + HI$ has been studied spectrophotometrically in a static system over the pressure ranges of PhCHO, 7-56 Torr, and I_2, 2-46 Torr. Over the temperature range 216-308°, the initial rate of disappearance of I_2 is first order in [PhCHO] and half order in $[I_2]$. These kinetics are consistent with $PhCHO + I\cdot \rightarrow Ph\dot{C}O + HI$ (1) as the rate-determining step, for which k_1 was found to be $\log (k_1, M^{-1}\,\mathrm{sec}^{-1}) = (10.08 \pm 0.16) - (16.69 \pm 0.36)/\theta$, where $\theta = 2.303RT$ kcal/mol. This leads to a benzaldehyde carbonyl C-H bond strength of 86.9 kcal/mol. From this activation energy, $\Delta H_f{}^\circ{}_{298}(Ph\dot{C}O)$ is calculated to be 26.1 ± 2 kcal/mol. This value is identical with the carbonyl C-H bond strength of formaldehyde and acetaldehyde. From thermochemical and esr data it is shown how stabilization of formyl radicals, $R\dot{C}O$, is independent of the R and may be explained by conjugation of the odd electron with one of the oxygen lone-pair electrons. In terms of the benzoyl radical, all evidence is consistent in that there is no contribution to the radical stability from structures in which the unpaired electron is conjugated with the aromatic ring.

Substitution of a phenyl group for a hydrogen atom in the methyl free radical results in substantial stabilization of the radical. A quantitative measure of this stabilization may be obtained from the C-H bond strength; defined as the heat of the reaction

$$RC{-}H \longrightarrow R\dot{C} + H\cdot$$

From the C-H bond strengths of 104 kcal/mol in methane and 85 kcal/mol in toluene,[2] a phenyl group stabilizes the radical by 19 kcal/mol compared to a hydrogen atom. With reference to the C-H bond strength in ethane of 98 kcal/mol,[2] the phenyl stabilization of the radical is 13 kcal/mol compared to a methyl group.

Substitution of a second or third phenyl group in methane reduces the C-H bond strength to approximately 76 kcal/mol.[2] The reduction of 9 kcal/mol from toluene is much less than the decrease of 19 kcal/mol on substitution of the first phenyl group. The marked reduction from the additivity of group stabilization may be explained by steric interaction between two phenyl groups. Owing to the interaction of ortho hydrogens, the unpaired sp^2 electron can be coplanar with the aromatic sp^2 electrons of only one phenyl group.

Substitution of an oxygen atom for the isoelectronic CH_2 group in ethylene reduces the C-H bond strength from 109 ± 2 kcal/mol in ethylene to 87 kcal/mol in formaldehyde.[3] On replacement of a hydrogen atom of formaldehyde by a methyl group, the bond strength is unchanged at 87 kcal/mol in acetaldehyde. This is a marked deviation from the saturated hydrocarbon series, where methyl substitution reduces the α-C-H bond strength of ethane by 3 kcal/mol.[3]

In benzaldehyde, we have substitution of a formaldehyde hydrogen atom by a phenyl group. From the discussion of the phenylmethane series, this might be expected to reduce the C-H bond strength. However, it must be noted that substitution of a methyl group had no effect, so that phenyl group stabilization of the formyl radical is by no means a forgone conclusion.

Literature values support analogy with the phenylmethane series and considerable stabilization of the benzoyl radical. From kinetic studies of the pyrolysis of benzil,[4] benzophenone,[5] benzoyl chloride,[6a] and benzoyl bromide,[6b] the C-H bond strength in benzaldehyde may be calculated to be 83, 82, 77, or 79 kcal/mol, respectively.

To reduce the uncertainty in the stabilization energy of the benzoyl radical, we report a kinetic study of the reaction of iodine atoms with benzaldehyde. This technique has been shown previously to yield accurate values of C-H bond strengths.[7]

Experimental Section

Materials. Mallinckrodt PhCHO was degassed and distilled on the vacuum line. The middle fraction, which was shown to be gas chromatographically pure, was stored under vacuum and used for kinetic runs. I_2 from Mallinckrodt was degassed at −10° and sublimed into a storage vessel attached to the heated inlet manifold. A sample of PhCIO was prepared by bubbling HI through a solution of PhCBrO.[8] The PhCIO was separated from unreacted PhCBrO by fractional vacuum distillation, but a colorless solution could not be obtained. Attempts to obtain a pure sample of PhCIO in the gas phase for quantitative ultraviolet spectral determinations were unsuccessful. The considerable darkening of the solution which occurred on standing was accelerated by warming the storage vessel in order to increase the vapor pressure, and a solid was deposited from the solution.

Apparatus. The absorption of the reacting species was measured with a Cary 15 spectrophotometer as described previously.[9] The

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reaction vessels were conditioned by the deposition of a coating of Teflon from the di-*tert*-butyl peroxide initiated polymerization of 120 Torr of C_2F_4 at 195°.

Procedure. The inlet manifolds and reaction vessel were evacuated to less than 10^{-4} Torr prior to a run. The desired pressure of PhCHO was added to the reaction vessel *via* the heated inlet manifold by warming the storage vessel. After pumping the PhCHO from the inlet manifold and pressure transducer, I_2 was added to the reaction vessel and the total pressure measured. The absorbance at 450, 490, or 500 nm in the visible and 285 or 290 nm in the ultraviolet was recorded on a synchronously driven chart. Absolute rates were obtained from optical density calibrations in the visible, where I_2 is the only absorbing species. The initial rate of change of absorbance at 285 or 290 nm was also measured. The gas-phase extinction coefficient of PhCIO was not available, so that the absorbance rate could not be converted directly to absolute reaction rates. However, the ratio of the absorbance rate at 285 or 290 nm to the absolute reaction rate measured in the visible was invariant at each temperature as the concentration of PhCHO was varied over a 7-fold range and that of I_2 over a 20-fold range. This is in essence a mass balance check, and therefore in the initial stages of the reaction there can be no change in the reaction stoichiometry.

The pressure of the reaction mixture was measured with a precision of better than 0.1 Torr by nulling both sides of a differential pressure transducer with He. The reaction vessel was momentarily opened to one side of the transducer and any small difference between the actual and estimated pressure measured on an oil manometer. During the time of the initial rate measurements at temperatures below 310°, no pressure change could be detected in the reaction mixture for $-\Delta I_2$ less than 0.5 Torr. However, with extended reaction time above 300°, a pressure increase was observed. Surprisingly, below 260° a reaction time of many hours produced a pressure decrease. This observation is discussed in a later section.

The reaction mixture was analyzed after condensation in a liquid-nitrogen-cooled trap. Small quantities of noncondensable gases were detected by opening the trap to the main vacuum manifold. The deflection of an ionization gauge above 10^{-4} Torr was sensitive to less than 0.01 Torr of noncondensable gas in the trap. It was found that no noncondensable gases were formed below 270° in the time of initial rate measurements, and only small amounts were detected in this time at 307°. Larger amounts of noncondensable gas were formed with longer reaction time and higher temperatures, but these results will be discussed elsewhere.[10] HI was distilled from the condensate by replacing the liquid nitrogen with an acetone–liquid nitrogen slush bath. A liquid fraction at room temperature was distilled from the condensate cooled in a salt–ice bath into a liquid-nitrogen-cooled cold finger.

The cold-finger fraction was analyzed as a liquid injection on a F and M Model 810 gas chromatograph using a flame ionization detector and a silicone oil column. From the runs with reaction temperatures less than 270° and short reaction times, there was only one prominent peak apart from PhCHO. This was shown to have the same retention time as the sample of PhCIO. No attempt was made to measure the amount of PhCIO, as undoubtedly the separation from I_2 in the salt–ice bath residue is inefficient. At temperatures above 300°, the formation of both PhH and PhI was observed in the gas chromatographic analysis. With extended reaction time (greater than 12 hr at 240° or greater than 1 hr above 300°), the presence of toluene was also detected in the sample analyzed by gas chromatography.

Results and Discussion

For the experimental conditions given in this paper, the reaction of I_2 with PhCHO is fully described by the scheme

$$I_2 \rightleftarrows 2I\cdot \quad K_{I_2}$$

$$PhCHO + I\cdot \rightleftarrows Ph\dot{C}O + HI \qquad (1)$$

$$Ph\dot{C}O + I_2 \rightleftarrows PhCIO + I\cdot \qquad (2)$$

Assuming the formation of I· is a fast preequilibrium by analogy with previous systems,[7] the rate of disappearance of I_2 is given by

$$\frac{-d[I_2]}{dt} = \frac{k_1 K_{I_2}^{1/2}[I_2]^{1/2}[PhCHO]}{1 + k_{-1}[HI]/k_2[I_2]}\left[1 - \frac{[PhCIO][HI]}{[PhCHO][I_2]K_{12}}\right] \qquad (I)$$

where K_{12} is the equilibrium constant for the overall reaction

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

From analogous systems, the value of k_{-1}/k_2 is approximately 0.1 and that for K_{12} approximately 0.01. In the initial stages of the reaction initiated from PhCHO and I_2, the ratios $[HI]/[I_2]$ and $[PhCIO][HI]/[PhCHO][I_2]$ are very small, so that eq I simplifies to

$$\frac{-d[I_2]}{dt} = k_1 K_{I_2}^{1/2}[I_2]^{1/2}[PhCHO] \qquad (II)$$

Values of $-d[I_2]/dt$ were obtained by graphically extrapolating the absorbance–time plots of the spectrometer charts to zero time. From the experimental results listed in Table I, values of k_1 were calculated by eq II. In some runs the rate of disappearance of I_2 was followed until it was half the initial rate. Values of $-d[I_2]/dt$ were determined at regular intervals from the slope of the tangent to the absorbance–time curve in the visible region of the spectrum. By assuming $-\Delta[I_2] = -\Delta[PhCHO] = \Delta[PhCIO] = \Delta[HI]$, the concentration of each species was calculated at each point. An initial estimate of k_1 and K_{12}, defined by eq I, was refined by computer until the least-squares deviation between calculated and experimentally measured values of $-d[I_2]/dt$ was a minimum.[11] Good agreement was obtained between calculated and experimental values of $-d[I_2]/dt$, as shown in Table II. Reactions 1 and 2 must

Table I. Rate Constants for the Reaction $PhCHO + I\cdot \rightarrow Ph\dot{C}O + HI$ (k_1)

Temp, °C	[PhCHO]$_0$, Torr	$[I_2]_0$, Torr	$10^4 \cdot (d[I_2]/dt)_0$, Torr sec^{-1}	$10^4 \cdot K_{I_2}^{1/2}$, Torr$^{1/2}$	$10^{-2}k_1$, M^{-1} sec^{-1}
217.2	18.1	21.8	1.06	1.07	3.6
217.1	21.2	5.5	0.77		4.4
216.6	23.8	5.1	0.75		4.4
216.6	55.8	8.5	1.92		3.4
216.6	37.9	17.7	2.40		4.3
216.7	8.6	18.9	0.68		5.1
239.9	18.2	6.2	3.36	2.46	9.6
240.2	38.9	28.6	13.7		9.6
240.3	9.0	26.8	2.83		7.9
240.5	22.6	4.6	3.29		8.9
240.5	55.2	2.2	6.48		10.3
263.8[a]	12.1	14.5	14.2	5.20	19.8
263.8[a]	12.1	14.5			23.3[b]
262.8[a]	16.2	19.3	20.6		18.7
262.0[a]	10.7	2.2	3.65		17.2
262.1[a]	23.4	46.6	49.6		20.0
262.1[a]	24.8	15.6	27.5		18.0
297.9	5.8	12.6	46.2	15.1	52.7
297.8	13.1	11.3	94.0		50.7
307.1	6.8	13.4	79.5	19.0	60.8
307.1	12.5	11.5	132.3		58.7
307.1	12.5	11.5			50.4[b]
307.1	10.9	3.6	71.4		65.8
307.1	10.9	3.6			55.0[b]

[a] Packed reaction vessel. [b] Computed from eq 1.

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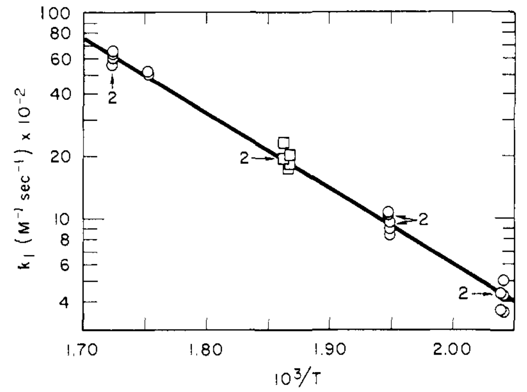


Figure 1. Arrhenius plot for the reaction $PhCHO + I\cdot \rightarrow Ph\dot{C}O + HI$ (k_1): □, rate constants obtained in the packed vessel; numbers indicate number of overlapping points.

be fully representative of the mechanism for at least one half-life.

Table II. Experimental and Calculated Values of $d[I_2]/dt$ by Eq I[a]

$-10^4 \cdot d[I_2]/dt$ (exptl), Torr sec^{-1}	$-10^4 \cdot d[I_2]/dt$ (calcd), Torr sec^{-1}	[PhCHO], Torr	$[I_2]$, Torr	[PhCIO], Torr	[HI], Torr
132	125	12.5	11.5	0.0	0.0
109	103	11.8	10.8	0.7	0.7
84.2	86.4	11.4	10.4	1.1	1.1
67.4	75.8	11.2	10.2	1.3	1.3
54.6	49.9	10.8	9.8	1.7	1.7

[a] 307.1°; k_1 (computed to minimize least-squares errors) = 0.149 $Torr^{-1}$ sec^{-1}; K_{12} (computed to minimize least-squares errors) = 0.055; k_{-1}/k_2 (assigned from ref 7) = 0.12.

Further evidence for the reaction scheme is obtained from the values of k_1 calculated from initial rates and eq II. Concentrations of PhCHO were varied over a 7-fold range and those for I_2 over a 20-fold range, but the values of k_1 were invariant within the experimental error.

Runs were also made in a reaction vessel packed with pieces of glass tubing so that the surface-to-volume ratio was eight times that of the unpacked vessel. This vessel was conditioned with C_2F_4 as described earlier. Rates measured in the packed vessel showed good agreement with those in the unpacked vessel, as may be seen from Figure 1.

Arrhenius parameters for k_1 were calculated from the least-squares line shown in Figure 1

$$\log (k_1, M^{-1}\ sec^{-1}) = (10.08 \pm 0.16) - (16.96 \pm 0.36)/\theta$$

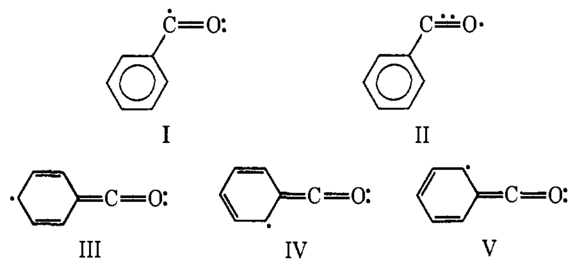
where $\theta = 2.303RT$ kcal/mol and the errors quoted are standard deviations. With the assumption that $E_{-1} = 1 \pm 1$ kcal/mol,[7] $\Delta E_{535} = 15.7 \pm 1.1$ kcal/mol. No $C_p°$ values have been reported for PhCIO, but we can estimate $\overline{\Delta C_p°} = (\Delta C_p°_{538} + \Delta C_p°_{298})/2$ from $\overline{\Delta C_p°}$ for the reaction $CH_3CHO + I\cdot \rightleftarrows CH_3CO + HI$. If we assume $\overline{\Delta C_p°}$ is the same for the two reactions, then $\overline{\Delta C_p°}$ for reaction 1 is -0.1 ± 0.5 gibbs/mol.[12] This yields $\Delta E_{298} = 15.7 \pm 1.1$ kcal/mol. This is equivalent to a PhCHO carbonyl C–H bond strength of 86.9 ± 1.1 kcal/mol. From the known heats of formation of the other species,[13,14] $\Delta H_f°_{298}(Ph\dot{C}O) = 26.1 \pm 2$ kcal/mol.

The Arrhenius A factor measured in this work for eq 1, $\log A_1 = 10.1$, is in good agreement with the values of 10.9 and 10.3 reported for the analogous reaction of iodine atoms with HCHO and CH_3CHO, respectively. The decrease in A factor with increase in size and mass of the aldehyde would suggest that the transition complex is similar in each case, the A factor differences being largely due to $\Delta S^{\neq}$ derived from translational and external rotational entropies.

The experimental value of 86.9 kcal/mol for the carbonyl C–H bond strength in PhCHO may be compared with the corresponding C–H bond strengths of 87 kcal/mol in HCHO and 87 kcal/mol in CH_3CHO.[7] There is no stabilization of the acyl radical due to substitution of a hydrogen atom by a methyl group or by a phenyl group. This result may appear surprising at first sight, but is consistent with available thermochemical and esr data.

The C–H bond strength in HCHO of 87 kcal/mol may be compared to 108 kcal/mol for the isoelectronic ethylene. This reduction of 21 kcal/mol may be ascribed to stabilization of the formyl radical by conjugation of the odd carbon electron with one of the lone-pair oxygen electrons. Furthermore, this stabilization energy of 21 kcal/mol is much greater than an alkyl stabilization of 3 kcal/mol obtained by comparison of the C–H bond strengths in ethane and isopropane, or 13 kcal/mol from comparison of the primary C–H bond strengths in ethane and toluene. In the formyl series, the radical stabilization is not additive. It is determined by the dominant factor, which is conjugation with the lone pair electrons.

Stabilization of the benzoyl radical may also be considered in terms of resonance structures I–V. In the previous discussion, we have postulated that the stabilization of the benzoyl radical is solely due to a contribution from structure II, with there being no contribution whatsoever from structures III, IV, or V. This is in good agreement with the possible gain in energy from forming the third C–O bond in II, compared to forming an additional phenyl-C bond in III–V. The π-bond energy may be defined as the heat of reaction in forming the bond from the hypothetical diradical.


I
II
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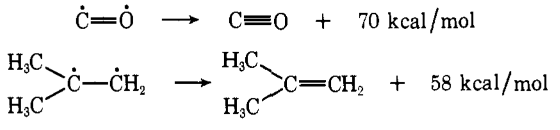

$$\dot{C}=\dot{O} \longrightarrow C\equiv O + 70\ \text{kcal/mol}$$

$$(H_3C)_2\dot{C}-\dot{C}H_2 \longrightarrow (H_3C)_2C=CH_2 + 58\ \text{kcal/mol}$$

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[14] J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, London, 1970.

The formation of an additional C–O bond compared to an additional C–C bond is favored by 12 kcal/mol. To this difference must be added about 12 kcal due to the decrease of aromatic stability in structures III–V.

The deductions from this paper are strongly supported by recent esr measurements of Krusic and Rettig.[15] They found that the major proton hyperfine splitting was due to the meta hydrogens. The ortho and para coupling constants for the benzyl and benzoyl radicals are incompatible, as seen from Table III, and support the lack of stabilization from structures III–IV. Furthermore, the major proton hyperfine splitting due to the meta hydrogen was rendered equivalent by a fast averaging process above −120°. The barrier for internal rotation is reduced from 7 kcal/mol in benzaldehyde[16] to approximately 3 kcal/mol in the radical. This reduction is inconsistent with the formation of a partial Ph–CO double bond. Both the unusually small *g* value and the very large ^{13}C splitting of the radical derived from benzaldehyde-*7*-^{13}C are further confirmation of the non-π nature of the benzoyl radical.[15]

Table III. Hyperfine Coupling Constants (G)

	Radical	
	Benzyl[a]	Benzoyl[b]
a_H(methylene)	16.4	
a_H(ortho)	5.1	<0.1
a_H(meta)	1.6	1.16
a_H(para)	6.3	<0.1

[a] From W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 4857 (1964). [b] From ref 15.

By restricting the measurements reported in this paper to the initial stages of the reaction, and to the temperature range 216–308°, we have avoided two possible complications which were briefly mentioned in the Experimental Section. The first of these is the unimolecular decomposition of the benzoyl radical.

$$\mathrm{Ph\dot{C}O \longrightarrow Ph\cdot + CO} \tag{3}$$

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

Reaction 3 occurs at a measurable rate in the iodine system above 300°, and these results will be reported elsewhere.[10] It does not interfere with rates measured from the initial disappearance of I_2, as it is irrelevant whether PhCIO or PhI is formed. However, at 290 nm, ϵ(PhCIO) > ϵ(PhI). As good agreement was obtained between initial rates measured in the ultraviolet and the visible, reaction 3 is negligible below 300°.

The other complication is the formation of toluene with long reaction time. Qualitative observations show this is accelerated by the presence of PhCIO and HI or an increase in the surface area. Whereas reaction 1 was unchanged by an eightfold increase in the surface to volume ratio, with similar experimental conditions the formation of toluene was more than doubled. It might be noted that no toluene could be detected in either vessel in the initial stages, and it was only with long reaction time that toluene was a prominent product. We suggest two possible mechanisms for the formation of toluene, both of which are most likely surface catalyzed. Staudinger and Anthes[3] have reported the condensation of PhCIO with PhCHO in the liquid phase.

$$\mathrm{PhCHO + PhCIO \rightleftarrows PhCHIOCOPh} \tag{5}$$

The ester would be expected to react with HI, as has been found in previous methyl ester–hydrogen halide systems.[17]

$$\mathrm{PhCHIOCOPh + HI \rightleftarrows PhCHI_2 + PhCOOH} \tag{6}$$

$PhCHI_2$ will yield $PhCH_3$ in the presence of iodine atoms and HI.

$$\mathrm{PhCHI_2 + 2HI \rightleftarrows PhCH_3 + 2I_2} \tag{7}$$

PhCHO and HI were stable at the lower temperatures in the absence of I_2 and PhCIO. This would suggest that reactions 8–10 do not contribute to the formation of $PhCH_3$.

$$\mathrm{PhCHO + HI \rightleftarrows PhCHIOH} \tag{8}$$

$$\mathrm{PhCIO + HI \rightleftarrows PhCI_2OH} \tag{9}$$

$$\mathrm{PhCHIOH + HI \rightleftarrows PhCHI_2 + H_2O} \tag{10}$$

In agreement with the above mechanism, the formation of toluene and iodine with a corresponding pressure decrease was observed with extended reaction time. Owing to the difficulty of separating the involatile products from I_2, no attempt was made to analyze the residue remaining in the salt–ice-cooled trap.

Conclusion

The value of $\Delta H_f{}^\circ{}_{298}(\mathrm{Ph\dot{C}O}) = 26.1 \pm 2$ kcal/mol is several kilocalories per mole less than the range of values reported in the literature. DH°(Ph(C–H)O) = 86.9 ± 1 kcal/mol measured in this work is identical with that found for DH°(H(C–H)O) and DH°(CH_3-(C–H)O). This similarity would suggest that stabilization of formyl radicals, R$\dot{C}$O, is independent of R and is determined solely by conjugation of the unpaired carbon electron with the lone-pair oxygen electrons. Resonance structures in which the unpaired carbon electron is conjugated with a phenyl ring make no contribution to the stability of the benzoyl radical.

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(16) W. G. Fately, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, **21**, 231 (1965); F. A. L. Anet and M. Ahmad, *J. Amer. Chem. Soc.*, **86**, 119 (1964).

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