stant with increase in ring size. The dominant mechanism must then be the direct radical–fluorine collision, with at most a minor contribution from the π systems.

BDPA behaves in a manner similar to GALV except that all ^{19}F enhancements with BDPA have larger scalar components. BDPA must also couple primarily with the ^{19}F directly, the larger scalar coupling resulting from a sterically more available unpaired electron on the radical.

The stronger scalar components in fluorine polarizations with DPPH cannot be readily explained solely on the basis of direct collision at the F site. Nevertheless, indirect scalar coupling *via* ring orbitals seems unlikely, since neither calculated nor observed ionization potentials for the two π systems can be correlated with the F polarizations.[5] A possible explanation for the DPPH results is longer lived collisions due to N–N attraction between radical and receptor molecules, but multifield DNP measurements would be required to assess this hypothesis.

In summary, DNP offers no evidence for spin coupling *via* either π system in $(PNF_2)_n$ with the three radicals tested. As a corollary, the ring π orbitals show no effects on the direct polarization of orbitals localized near fluorine. To a large extent, the exocyclic F atoms in $(PNF_2)_n$ behave toward radical probes as though they were not conjugated to the ring π orbitals. This situation is in marked contrast to that of F in fluorobenzenes or Cl in phosphonitrilic chlorides.

Acknowledgment. One of us (J. A. P.) acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are grateful for the high-field nmr spectra obtained by Dr. D. Denney.

Photochemistry of Benzaldehyde

Michael Berger, Irwin L. Goldblatt, and Colin Steel*

*Contribution from the Department of Chemistry,
Brandeis University, Waltham, Massachusetts 02154.* *Received July 6, 1972*

Abstract: The photochemistry of benzaldehyde has been studied by determining the quantum yields of benzene and carbon monoxide formation, benzaldehyde consumption and phosphorescence emission, and by following the phosphorescence lifetime over a range of pressure and excitation wavelengths. These data together with information from triplet transfer studies allow the construction of a model for the primary photochemical–photophysical processes (Figure 9) and the determination of most of the primary rate constants (Table II). Excitation with 276-nm light, $S_0 \rightarrow S_2$, results in the population of two vibrationally excited triplet states. At low pressures dissociation, yielding benzene and CO, occurs from the high vibrational levels of these states. Collisional deactivation of these states feeds the lower vibrational levels of the lowest triplet; from here there are no chemical decay channels and phosphorescence can be observed. In contrast to $S_0 \rightarrow S_2$ excitation, $S_0 \rightarrow S_1$ excitation results in no benzene or carbon monoxide formation and the phosphorescence yields are insensitive to pressure. There is however a significant quantum yield of benzaldehyde consumption and polymer formation can be observed.

As part of our work on the gas-phase photochemistry of azoalkanes[1] we have used benzaldehyde as a triplet energy donor.[2] Benzaldehyde is one of the few molecules which exhibits a strong phosphorescence in the gas phase,[3,4] and we believed that this emission would provide a very convenient monitor. Other workers have also used benzaldehyde as a triplet energy donor in the gas phase[5a] and in solution.[6,7] Our use of benzaldehyde as an energy donor was hampered by our lack of understanding of the photochemistry of benzaldehyde itself.

There were rather preliminary studies into the direct photolysis of gaseous benzaldehyde.[8–11] It has been reported that n $\rightarrow$ π^* excitation in the gas phase results in polymer formation and that at elevated temperatures the quantum yield of benzaldehyde consumption was as high as 40.[11] It has also been reported that at wavelengths below 270 nm benzaldehyde decomposed into benzene and carbon monoxide.[10]

The aim of this work was to obtain absolute quantum yields of the primary photophysical and photochemical processes and to study the effect of wavelength on the system. In this way we hoped to determine the mechanism for the population of the emitting state and determine from which state(s) dissociation into benzene and carbon monoxide occurred.

Experimental Section

Materials. All reagents were the best grade commercially available. The preparations of azoisopropane (AIP), 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH), and 2,3-diazabicyclo[2.2.2]oct-2-

---

(1) W. Clark and C. Steel, *J. Amer. Chem. Soc.*, **93**, 6347 (1971).

(2) A preliminary account of the work reported in this paper was presented by I. L. Goldblatt and C. Steel, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., 1969.

(3) P. Longin, *C. R. Acad. Sci.*, **255**, 865 (1962).

(4) M. Stockburger, *Z. Phys. Chem.* (*Frankfurt am Main*), **31**, 350 (1962).

(5) (a) G. R. De Maré, P. Goldfinger, G. Huybrects, E. Jonas, and M. Toth, *Ber. Bunsenges. Phys. Chem.*, **73**, 867 (1969). (b) G. R. De Maré, M. C. Fontaine, and M. Termonia, *Chem. Phys. Lett.*, **11**, 617 (1971).

(6) N. C. Yang, *Photochem. Photobiol.*, **7**, 767 (1968).

(7) N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, **90**, 3264 (1968).

(8) F. Almasy, *J. Chem. Phys.*, **30**, 528, 634, 713 (1933).

(9) G. R. De Maré, M. C. Fontaine, and P. Goldfinger, *J. Org. Chem.*, **33**, 2528 (1968).

(10) (a) M. de Hemptinne, *J. Phys. Radium*, **9**, 357 (1929); (b) *C. R. Acad. Sci.*, **186**, 1295 (1928).

(11) F. E. Blacet and D. Vanselow, Abstracts, 131th National Meeting of the American Chemical Society, Miami Beach, Florida, 1957.

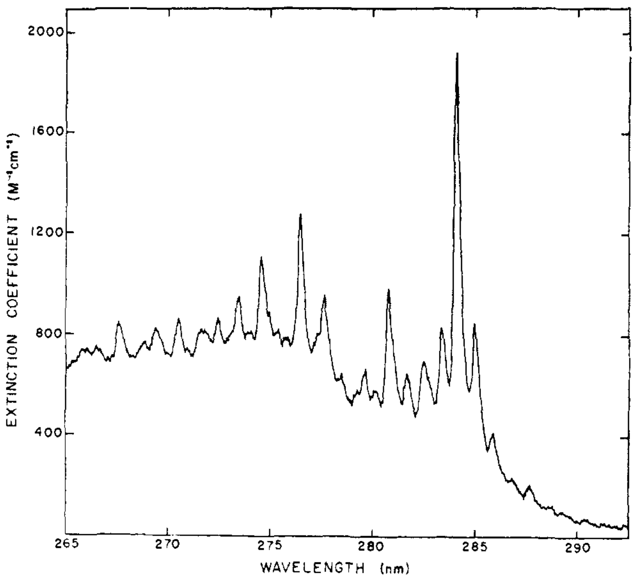
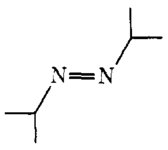
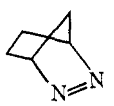


Figure 1. Gas-phase absorption spectrum of benzaldehyde in the 265–290-nm region.

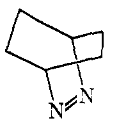
ene (DBO) have been described previously.[1] Benzaldehyde was



AIP



DBH



DBO

distilled and then purified by 4–5 trap vacuum distillation before use, and kept at −78° between experiments.

Apparatus. General descriptions of the photolysis, the emission, and the lifetime equipment have already been given.[1,12] The methods used to estimate decomposition and emission quantum yields are also to be found in these references. Most photolyses were carried out using cylindrical quartz optical cells 100 mm long and 22 mm in diameter. Photolyses were effected with a high-pressure mercury arc (PEK 100 W) in conjunction with a monochromator (Bausch amd Lomb) set so that the spectral bandwidth was 1.6 nm. For emission and lifetime measurements rectangular 10-mm path length fluorescence cells (Pyrocell) were used. Unless stated otherwise, all experiments were conducted at room temperature, 22 ± 2°.

Because of the adsorptive nature of the components great care had to be exercised in making up the gaseous mixtures. For the photolyses in which benzaldehyde alone was employed, Table I, the compound was vaporized directly into the reaction vessel and the pressure read on a spiral Bourdon gauge (Texas Instruments) after allowing sufficient time for equilibration. Whenever possible, absorption spectra were run before and after photolysis so that the quantum yield of benzaldehyde consumption could be determined. Analysis for the benzene and carbon monoxide evolved was carried out by gas chromatography, the extent of photolysis being generally kept below 5%.

Spectra. Absorption spectra, Figures 1 and 2, were run on a Cary 14 spectrophotometer. Because of the highly structured nature of the absorption in the 270–286-nm region the spectra were very sensitive to the spectral band width used. The spectra shown were recorded at a spectral band width of 0.8 Å. In determining emission yields the phosphorescence excitation spectra were generally recorded using a spectral band width of 1.8 nm for the excitation monochromator and 5 nm for the emission monochromator. The excitation spectrum tallied very well with the absorption spectrum, while the emission spectrum agreed excellently with those already reported for the phosphorescence of benzaldehyde.[4,13]

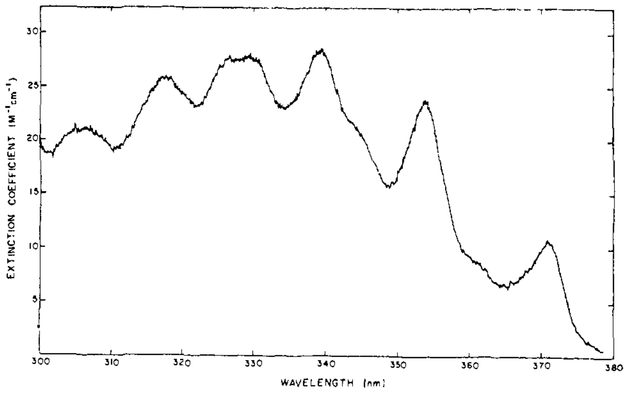


Figure 2. Solution-phase absorption spectrum of benzaldehyde in the n → π* region.

Table I. Quantum Yields in the Photolysis of Benzaldehyde

P_{PhCHO}, Torr	λ_{excit}, nm	Φ_{iiec}- (−PhCHO)	Φ_{dec}- (C_6H_6)	Φ_{dec}- (CO)
0.010	276		0.89	
0.021	276		0.94	
0.047	726		0.93	
0.051	276		0.71	
0.065	276		0.54	
0.075	276		0.58	
0.091	276		0.58	
0.100	276		0.57	
0.154	276		0.41	0.41
0.154	276		0.38	
0.172	276		0.36	0.39
0.201	276		0.38	0.29
0.207	276	0.38	0.36	0.31
0.307	276	0.36	0.35	
0.359	276	0.39	0.35	
0.622	276	0.35	0.33	0.33
0.025	284		0.87	
0.043	284		0.42	
0.065	284		0.29	
0.092	284		0.26	
0.151	284	0.38	0.20	
0.154	284	0.41	0.21	
0.207	284	0.38	0.18	0.18
0.307	284		0.20	
0.409	284		0.20	
0.622	284	0.34	0.17	0.16
0.046	328	0.39	0.006	<0.002
0.183	328	0.41	0.002	<0.002
0.567	328	0.41	0.002	<0.002
0.039	365	0.36	0.001	<0.002
0.175	365	0.41	0.0005	<0.002
0.372	365	0.43	0.0008	<0.002

Quantum Yields. The very low benzaldehyde pressures used in many of the experiments prevented a direct measurement of the fraction of light absorbed by the benzaldehyde. Thus most quantum yield determinations relied on a knowledge of the extinction coefficient of benzaldehyde as a function of wavelength. Because of the highly structured nature of the absorption in the 276- and 284-nm regions the absolute quantum yields of emission and decomposition are probably not known to better than 15% for these wavelengths. For n → π* absorptions we used literature extinction coefficients determined at 120°.[4] The n → π* transition is weak and the extinction coefficients are not known to better than 5–10%. Thus although the internal consistency of a set of data was generally better than 10%, the absolute values are probably not reliable to more than 15%.

---

(12) B. Soloman, T. Thomas, and C. Steel, *J. Amer. Chem. Soc.*, **90**, 2249 (1968).

(13) Y. Kanda, H. Kasida, and T. Matumura, *Spectrochim. Acta*, **20**, 1387 (1964).

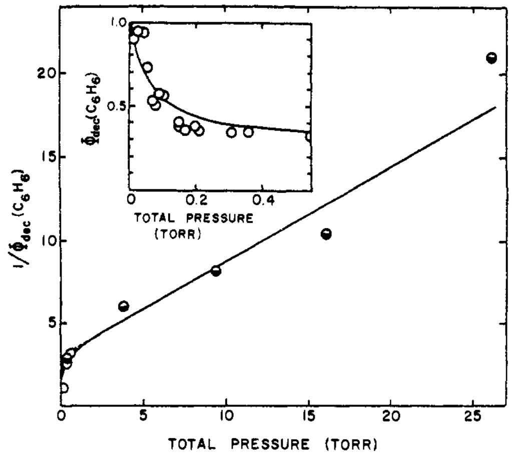


Figure 3. Quantum yield of benzene formation as a function of total pressure in the photolysis of benzaldehyde, λ_{excit} 276 nm: (○) benzaldehyde alone, (◒) 0.15 Torr of benzaldehyde + C_2H_6 as added gas. The solid curves are model curves calculated from eq I and the values of the optimized constants given in Table II.

Symbolism. In reporting quantum yields a left superscript T indicates that a triplet sensitized yield is referred to. The right subscript gives information as to the type of process being monitored, thus dec stands for decomposition, em for emission, etc. The term in parentheses is the quantity being measured, thus $\Phi_{dec}(-\text{PhCHO})$ refers to the quantum yield of benzaldehyde decomposition monitored by measuring the benzaldehyde consumption. Occasionally the wavelength (nm) of the exciting radiation is given as a right superscript.

Results and Discussion

(1) Absorption Spectrum. The gas-phase absorption spectrum in the 265–295-nm region is shown in Figure 2. The low intensity band in the 300–380-nm region has been assigned to an n → π^* ($^1A' \rightarrow {}^1A''$) transition.[14] Because of the low extinction coefficient in this region and the low vapor pressure of benzaldehyde it is hard to obtain a good gas-phase n → π^* spectrum of benzaldehyde. But the solution-phase spectrum shown in Figure 2 closely resembles the reported gas-phase n → π^* spectrum at 120°,[4] and is also in agreement in the other reported solution spectra.[15,16] The next band which starts at about 284 nm has been assigned to a $\pi \rightarrow \pi^*$ ($^1A' \rightarrow {}^1A'$) transition by Inuzuka and Yokota[17] and to a perturbed $^1A' \rightarrow {}^1L_b$ transition by Nagakura and by Goodman.[18,19] This band is probably composed of more than one vibrational progression as evidenced by a change in polarization within the band.[19] Vacuum ultraviolet spectra have also been reported.[18]

(2) Photolysis at 276 nm. From the data shown in Table I and Figure 3 it can be seen that at very low pressures the quantum yield of benzene formation, $\Phi_{dec}(C_6H_6)$, equals $\Phi_{dec}(-\text{PhCHO})$, the quantum yield of benzaldehyde consumption, and that the benzene and carbon monoxide are formed in a 1:1 ratio. From the sharp break in the $1/\Phi_{dec}(C_6H_6)$ *vs.* pressure curve it can be inferred that there are two states forming benzene, one of which is longer lived than the other.

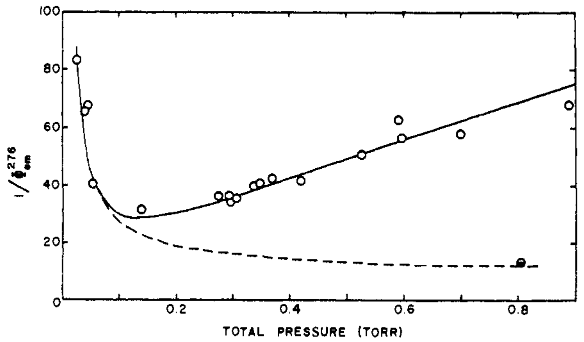


Figure 4. Variation in quantum yields of benzaldehyde phosphorescence with total pressure, λ_{excit} 276 nm: (○) benzaldehyde alone, (◒) 0.05 Torr of benzaldehyde + C_2H_6 as added gas. The solid curve is the model curve for benzaldehyde alone calculated from eq IV and the optimized constants given in Table II. The dashed curve is the model curve for added ethane.

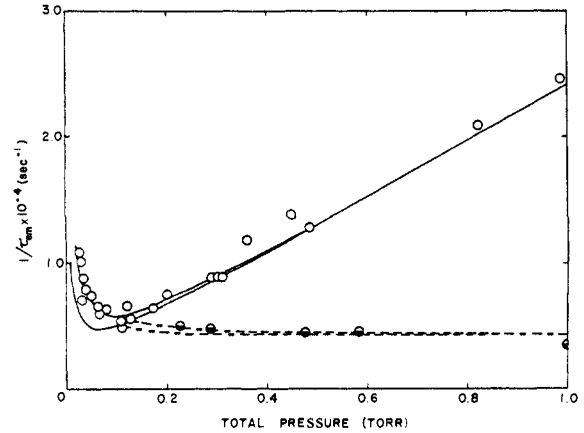


Figure 5. Variation in the emission lifetime, τ_{em}, of benzaldehyde with total pressure: (○) benzaldehyde alone, (◒) 0.10 Torr of benzaldehyde + C_2H_6 as added gas. The solid curves are model curves calculated from eq III and the optimized constants given in Table II except for *D*. The upper curve refers to $D = 17.2 \times 10^{-4}\ M\,\text{cm}^2\,\text{sec}^{-1}$, the lower curve to $D = 8.5 \times 10^{-4}\ M\,\text{cm}^2\,\text{sec}^{-1}$. The dashed curves are calculated from eq III in which the fourth term has been changed to $6D/([\text{PhCHO}] + [C_2H_6] + 0.81 \times 10^{-7})$.

As the benzene yield decreases in the 0–0.2-Torr region, there is a concomitant increase in the phosphorescence yield, see Figure 4. In the higher pressure region, >0.2 Torr, the quantum yield of benzene continues to decrease, Figure 3. If the pressuring is carried out with benzaldehyde alone, then both the emission lifetime and the yield decrease, Figures 4 and 5. This decrease is due to self-quenching of the benzaldehyde phosphorescence. If an "inert" gas like ethane is used, then the emission yield and the lifetime change only very slowly. Above 1 Torr of added ethane the decrease in the benzene yield continues and the emission yield continues to increase slowly until the pressure reaches 10 Torr. However in this region the emission lifetime is invariant, Figure 6.

(3) DBH as a Triplet Counter. Benzaldehyde phosphorescence is readily quenched by azoalkanes through exchange-induced resonance energy transfer.[1,20] DBH is a particularly convenient azo compound since the yields of C_5 hydrocarbon and N_2 from triplet DBH are unity.[1,21] A Stern–Volmer plot for quenching by

---

(14) J. M. Hollas, E. Gregorek, and L. Goodman, *J. Chem. Phys.*, **49**, 1745 (1968).

(15) F. Dörr, *Z. Elektrochem.*, **61**, 950 (1957).

(16) J. R. Majer, S-A. M. A. Naman, and J. C. Robb, *Trans. Faraday Soc.*, **65**, 1846 (1969).

(17) K. Inuzuka and T. Yokota, *Bull. Chem. Soc. Jap.*, **38**, 1055 (1965).

(18) K. Kimura and S. Nagakura, *Theor. Chem. Acta*, **3**, 164 (1965).

(19) R. Shimada and L. Goodman, *J. Chem. Phys.*, **43**, 2027 (1965).

(20) C. Steel and K. R. Naqvi, *Chem. Phys. Lett.*, **6**, 29 (1970).

(21) P. S. Engel, *J. Amer. Chem. Soc.*, **91**, 6903 (1959).

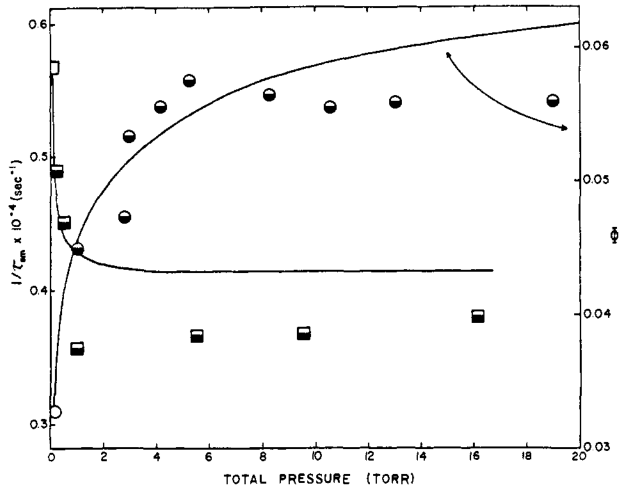


Figure 6. Variation in the emission lifetime, τ_{em}, and the phosphorescence yield, $\Phi_{em}{}^{276}$, of benzaldehyde as a function of added ethane: (○) 0.2 Torr of benzaldehyde, (◒) 0.2 Torr of benzaldehyde + added C_2H_6, (□) 0.1 Torr of benzaldehyde, (⬓) 0.1 Torr of benzaldehyde + added C_2H_6. The solid curves are model curves calculated from eq III and IV and the values of the optimized constants given in Table II.

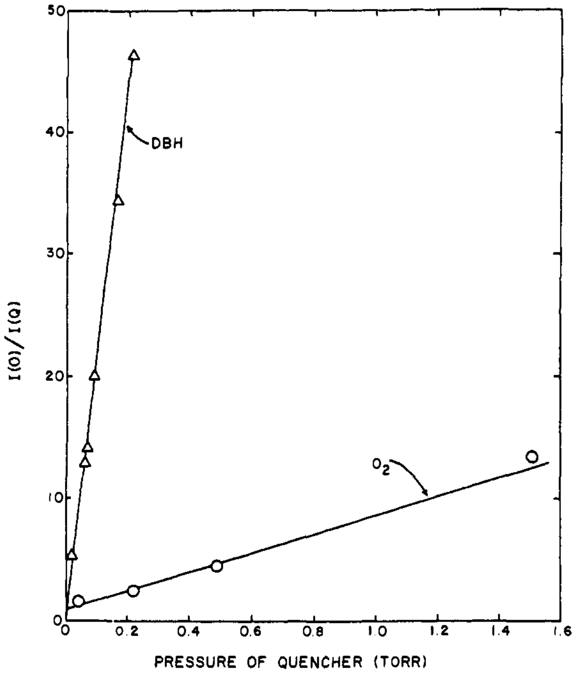


Figure 7. Quenching of benzaldehyde phosphorescence at 20° by DBH and O_2, P_{PhCHO} = 0.13 Torr, λ_{excit} 276 nm.

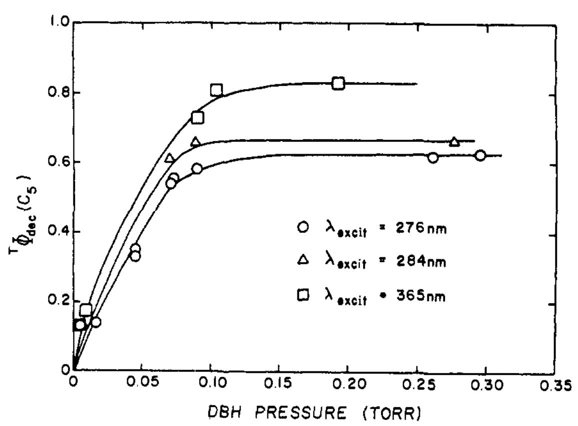


Figure 8. Quantum yield of C_5 formation *vs.* DBH pressure for benzaldehyde-sensitized decomposition of DBH.

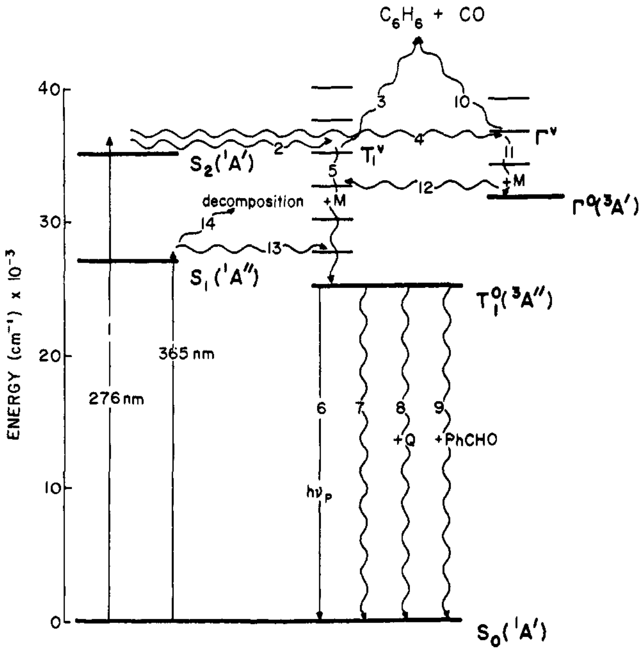


Figure 9. Model for photolysis of benzaldehyde; numerical values for the rate constants are given in Table II.

DBH is shown in Figure 7 where quenching by O_2 is also shown for comparison. In Figure 8 we plot $^{T}\Phi_{dec}(C_5)$ the quantum yield of the benzaldehyde-sensitized decomposition of DBH.

(4) A Model for 276-nm Photolysis. (a) Benzene Quantum Yields. In Figure 9 we present a model to explain our results. After excitation, reaction 1, there are rapid intersystem crossings to $T_1{}^v$ and Γ^v, reactions 2 and 4. The long-lived state is identified with $T_1{}^v$ and the short-lived one with Γ_v. By extrapolating the linear high-pressure portion of the $1/\Phi_{dec}(C_6H_6)$ *vs.* pressure curve back to zero pressure we estimate that the yield of C_6H_6 from Γ^v when there is no deactivation is ~0.32. This we identify with $\Phi_{isc}(\Gamma^v) = k_4/(k_2 + k_4)$, the quantum yield of Γ^v. Thus, $\Phi_{isc}(T_1{}^v)$, the yield of $T_1{}^v = k_2/(k_2 + k_4)$, is 0.68. In terms of the model then

$$\Phi_{dec}(C_6H_6) = \Phi_{isc}(T_1{}^v)\frac{k_3}{k_3 + k_5[M]} + \Phi_{isc}(\Gamma^v)\frac{k_{10}}{k_{10} + k_{11}[M]} \quad (I)$$

where the terms $k_3/(k_3 + k_5[M])$ and $k_{10}/(k_{10} + k_{11}[M])$ are the fractions of $T_1{}^v$ and Γ^v molecules which dissociate to benzene and CO. [M] is the total concentration of benzaldehyde plus any added gas.

At pressure <0.2 Torr we have

$$\Phi_{dec}(C_6H_6) \approx \Phi_{isc}(T_1{}^v)\frac{k_3}{k_3 + k_5[M]} + \Phi_{isc}(\Gamma^v)$$

while in the high-pressure regions

$$\Phi_{dec}(C_6H_6) \approx \Phi_{isc}(\Gamma^v)\frac{k_{10}}{k_{10} + k_{11}[M]}$$

Using the value of the collision-controlled rate constant, $1.8 \times 10^{11}\ M^{-1}\ \mathrm{sec}^{-1}$, for k_5 and the low-pressure data given in Figure 3, the low-pressure equation yields a value $\approx 4 \times 10^5\ \mathrm{sec}^{-1}$ for k_3. This rate constant is considerably greater than the radiative rate constant k_6 which has a value of about $4 \times 10^2\ \mathrm{sec}^{-1}$, *vide infra*, so it is clear why there is essentially no emission from T_1^{v}.

(b) Triplet Character of the Long-Lived State. By labeling the state which is intercepted at low pressures T_1^{v} we have implicitly assumed it to be a triplet. Is this assumption justified? The observed lifetime, $\tau_{\mathrm{em}}(\theta)$, of a "compound" state[22] θ will be given by

$$1/\tau_{\mathrm{em}}(\theta) \approx 1/\Phi_{\mathrm{em}}(\theta)[f_{\mathrm{S}}/\tau^0(\mathrm{S}) + f_{\mathrm{T}}/\tau^0(\mathrm{T})] \quad \text{(II)}$$

where f_{S} and f_{T} are the fractions of $\langle \mathrm{S} \rangle$ and $\langle \mathrm{T} \rangle$ character in θ; $\tau^0(\mathrm{S})$ and $\tau^0(\mathrm{T})$ are the radiative lifetimes of these states and $\Phi_{\mathrm{em}}(\theta)$ is the emission yield from θ.[23] If we identify θ with the long-lived state, then we see from Figures 4 and 5 that when $\tau_{\mathrm{em}} \approx 10^{-4}$ sec, $\Phi_{\mathrm{em}}{}^{276} \approx 0.01$. From the benzaldehyde absorption spectrum we know, using the Strickler–Berg equation,[24] $\tau^0(\mathrm{S}_1) \approx 2 \times 10^{-6}$ sec, $\tau^0(\mathrm{S}_2) \approx 1 \times 10^{-8}$ sec while from the phosphorescence yield and lifetime for the glass we know $\tau^0(\mathrm{T}_1) = 1/k_6 \approx 0.29 \times 10^{-2}$ sec.[25] By identifying S_1 or S_2 with $\langle \mathrm{S} \rangle$ and T_1 with $\langle \mathrm{T} \rangle$ and substituting into eq II it can readily be seen that θ can have little if any singlet character. Therefore the identification of the long-lived state with T_1 seems to be justified.

(c) Triplet Character of the Short-Lived State. We now turn our attention to the high-pressure region where we have the following major facts to explain. (1) The shape of the emission spectrum is invariant with pressure but the emission yield continues to increase slowly, Figure 6. (2) The emission lifetime is invariant, Figure 6. (3) The benzene yield continues to decrease, Figure 3. In general terms a state that is shorter lived than T_1^{v} must be dissociating to form benzene and CO and is collisionally deactivated only in the high-pressure region. Also the fact that the emission lifetime is essentially invariant in this region while the emission yield increases, Figure 6, shows quite clearly that this state must on collisional deactivation feed the emitting state T_1^0. In Figure 9, we have labeled this state Γ^{v}; we now inquire into its properties.

We can see no distinct emission from it and rather conservatively write $\Phi_{\mathrm{em}}{}^{276}(\Gamma^{\mathrm{v}}) < 10^{-3}$. Now the lifetime of this state, $\tau(\Gamma^{\mathrm{v}})$, can be estimated from the pressure behavior of the benzene quantum yield in the high-pressure region, Figure 3. In this region we know $1/\Phi_{\mathrm{dec}}(\mathrm{C_6H_6}) \approx 1/\Phi_{\mathrm{isc}}(\Gamma^{\mathrm{v}})\{1 + (k_{11}/k_{10})[\mathrm{M}]\}$. Again identifying k_{11} with the collision-controlled rate constant we obtain as a first estimate from the high-pressure slope of $1/\Phi_{\mathrm{dec}}(\mathrm{C_6H_6})$ *vs.* [M] in Figure 3 a value of $5 \times 10^7\ \mathrm{sec}^{-1}$ for k_{10}. Again substituting into eq II we see that Γ^{v} can have little singlet character. At present therefore we feel that the state is probably more or less a "pure" triplet and subsequently refer to this state as $\mathrm{T_x}$.

(d) Emission Lifetimes. Because of scatter from the exciting source emission measurements were started at least 50 μsec after the initiation of the flash. It can readily be shown that under these conditions there should be no appreciable signal from T_1^{v} or T_x^{v} molecules, the only contribution being from the longer-lived T_1^0 molecules. In the case of benzaldehyde alone therefore we should have $1/\tau_{\mathrm{em}} = k_6 + k_7 + k_9[\mathrm{PhCHO}]$. This equation, however, has omitted a term which becomes important at low pressures, namely, diffusion to the wall. Benzaldehyde is a very "sticky" molecule and it is likely that every wall encounter of an excited T_1^0 molecule will lead to deactivation. It has been shown that diffusion to the wall is an important source of deactivation of triplet biacetyl at low pressures.[26] From random walk theory we have $t_{\mathrm{diff}} = d^2/6\mathfrak{D}$ where t_{diff} is the time for a particle with diffusion coefficient $\mathfrak{D}$ to migrate a mean squared distance d^2.[27a] $\mathfrak{D}$ was calculated using standard formulas.[27b] Using a diameter of 6.8 Å for benzaldehyde we estimate $\mathfrak{D}$ (cm²/sec) $\approx D/[\mathrm{PhCHO}]$ where $D = 12 \times 10^{-4}\ M\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$. However the mean free path cannot be greater than the dimensions of the vessel. In other words there is always an effective "wall pressure" which we estimate at $\sim 1.5 \times 10^{-3}$ Torr $= 0.81 \times 10^{-7}\ M$. Thus finally $\mathfrak{D} \approx D/\{[\mathrm{PhDHO}] + 0.81 \times 10^{-7}\}$. For $d = 1$ cm we have $1/t_{\mathrm{diff}} \approx 6D/\{[\mathrm{PhCHO}] + 0.81 \times 10^{-7}\}$. This should give a measure of the rate at which a benzaldehyde T_1^0 molecule is quenched by collision with the wall. Thus the formula for the emission lifetime becomes

$$1/\tau_{\mathrm{em}} = \{k_6 + k_7\} + k_9[\mathrm{PhCHO}] + 6D/\{[\mathrm{PhCHO}] + 0.81 \times 10^{-7}\} \quad \text{(III)}$$

At pressures above 0.2 Torr the third term becomes small so that k_9 and $\{k_6 + k_7\}$ can be estimated from the slope and intercept, respectively, of the straight line portion of the curve. In this way we estimate as a first approximation $(k_6 + k_7) \approx 3 \times 10^3$ and $k_9 \approx 3.7 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$.

(e) Emission Quantum Yields. The fraction of T_1^{v} molecules which are deactivated is $k_5[\mathrm{M}]/\{k_3 + k_5[\mathrm{M}]\}$ while the corresponding fraction for T_x^{v} molecules is $k_{11}[\mathrm{M}]/\{k_{10} + k_{11}[\mathrm{M}]\}$. Thus the quantum yield of emission as a fraction of pressure should be given by eq IV. The last term in brackets represents

$$\Phi_{\mathrm{em}}{}^{276} = \left\{\Phi_{\mathrm{isc}}(\mathrm{T_1}^{\mathrm{v}})\frac{k_5[\mathrm{M}]}{k_3 + k_5[\mathrm{M}]} + \Phi_{\mathrm{isc}}(\mathrm{T_x}^{\mathrm{v}})\frac{k_{11}[\mathrm{M}]}{k_{10} + k_{11}[\mathrm{M}]}\right\} \times \left\{\frac{k_6}{k_6 + k_7 + k_9[\mathrm{PhCHO}] + \dfrac{6D}{[\mathrm{M}] + 0.81 \times 10^{-7}}}\right\} \quad \text{(IV)}$$

---

(22) J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Advan. Photochem.*, 7, 149 (1969).

(23) Consider a compound state $\theta = a\mathrm{S} + b\mathrm{T}$. For a radiative transition $\theta \rightarrow \mathrm{S_0}$, $1/\tau^0(\theta)$ will be proportional to

$$|\langle\theta|\mathrm{r}|\mathrm{S_0}\rangle|^2 = |\langle a\mathrm{S} + b\mathrm{T}|\mathrm{r}|\mathrm{S_0}\rangle|^2 = a^2|\langle\mathrm{S}|\mathrm{r}|\mathrm{S_0}\rangle|^2 + b^2|\langle\mathrm{T}|\mathrm{r}|\mathrm{S_0}\rangle|^2 + 2ab\langle\mathrm{S}|\mathrm{r}|\mathrm{S_0}\rangle\langle\mathrm{T}|\mathrm{r}|\mathrm{S_0}\rangle$$

If $\tau^0(\mathrm{S})$ and $\tau^0(\mathrm{T})$ are the radiative lifetimes of S and T, $1/\tau^0(\mathrm{S})$ and $1/\tau^0(\mathrm{T})$ will be proportional to $|\langle\mathrm{S}|\mathbf{r}|\mathrm{S_0}\rangle|^2$ and $|\langle\mathrm{T}|\mathbf{r}|\mathrm{S_0}\rangle|^2$, respectively. The absolute value of the third term in the above equation must be less than the sum of the first two terms. Thus $1/\tau^0(\theta) \approx f_{\mathrm{S}} \cdot 1/\tau^0(\mathrm{S}) + f_{\mathrm{T}} \cdot 1/\tau^0(\mathrm{T})$ where $f_{\mathrm{S}} = a^2$ and $f_{\mathrm{T}} = b^2$ are the fractions of S and T character in θ.

(24) S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 37, 814 (1962).

(25) V. L. Ermolaev, *Usp. Fiz. Nauk*, 80, 3 (1963); English translation, *Sov. Phys. Usp.*, 6, 333 (1963).

(26) (a) C. S. Parmenter and H. M. Poland, *J. Chem. Phys.*, 51, 1151 (1969); (b) H. W. Sidebottom, C. C. Badcock, J. G. Calvert, B. R. Rabe, and E. K. Damon, *J. Amer. Chem. Soc.*, 94, 13, (1972).

(27) (a) P. J. Wagner and I. Kochevar, *ibid.*, 90, 2232, (1968); (b) W. Kauzmann, "Kinetic Theory of Gases," W. A. Benjamin, New York, N. Y. 1966, p 204.

the fraction of T_1 molecules which emit. For benzaldehyde alone [M] = [PhCHO]. The rate constants k_3 and k_{10} have already been obtained from the benzene yield data and the constants k_5 and k_{11} have been assigned there, too. D, k_9, and $(k_6 + k_7)$ were determined from the lifetime data. However eq IV allows a separation of k_6 and k_7 because at pressures above 0.2 Torr and below 1.0 Torr the term in the first brackets can be approximated by $\Phi_{\text{isc}}(T_1^{\text{v}})$. Therefore in this pressure region

$$1/\Phi_{\text{em}}^{276} \approx \frac{k_6 + k_7}{k_6\Phi_{\text{isc}}(T_1^{\text{v}})} + \frac{k_9[\text{PhCHO}]}{k_6\Phi_{\text{isc}}(T_1^{\text{v}})}$$

Knowing k_9 and $\Phi_{\text{isc}}(T_1^{\text{v}})$ we can obtain k_6 and k_7 from the slope and intercept of the curve. The values so obtained were 3×10^2 and 3×10^3 sec^{-1}, respectively.

(f) **Optimization of Rate Constants.** In Table II we have gathered together the rate constants obtained for the benzene yield, the emission yield, and the lifetime data. Having these values and eq I, III, and IV we are now in a position to derive model curves to fit the experimental data over the entire pressure region, and make adjustments to the values of the constants. The optimized constants are given in Table II; using these "best" constants we have calculated the model curves shown in Figures 3–6.

Table II. Constants Obtained from the Photolysis of Benzaldehyde

Constant	Initial value[a]	Optimized value[a]
k_2/k_4	2.12[b]	2.12[b]
D	17.2×10^{-4} M cm^2 sec^{-1}	17.2×10^{-4} M cm^2 sec^{-1}
k_3	4.0×10^5 sec^{-1}	4.5×10^5 sec^{-1}
k_5	1.8×10^{11}	1.75×10^{11}
k_6	3×10^2 sec^{-1}	4.2×10^2 sec^{-1}
k_7	3×10^3 sec^{-1}	1.5×10^3 sec^{-1}
k_8 (DBH)		2.3×10^{10}
k_8 (AIP)		4.0×10^{10}
k_8 (DBO)		5.4×10^{10}
k_8 (O_2)		0.29×10^{10}
k_9	3.7×10^8	4.1×10^8
k_{10}	5×10^7 sec^{-1}	5.2×10^7 sec^{-1}
k_{11}	1.8×10^{11}	1.75×10^{11}
k_{12}	$<5 \times 10^7$ sec^{-1}	$<5 \times 10^7$ sec^{-1}
k_{13}/k_{14}	5.7[b]	5.7[b]

[a] M^{-1} sec^{-1} except where noted. [b] Dimensionless.

It is interesting to note that the approximate values are very similar to the optimized values except for k_6 and k_7 which depend on the intercept of the $1/\Phi_{\text{em}}$ *vs.* pressure plot. In forcing the data to fit a straight line (as is done in the initial treatment of the data), one weights the lower pressure points too heavily; at pressures even above 0.15 Torr, there is significant curvature caused by the diffusional effect which makes $1/\Phi_{\text{em}}$ larger than when diffusion can be ignored. Thus the straight-line intercept one obtains is actually too high.

(g) **Emission Yields and Lifetimes in the High-Pressure Region.** We have already observed that the benzene yield continues to decrease in the high pressure region, $P_{\text{tot}} > 1$ Torr. This is mainly associated with deactivation of molecules in the short-lived state T_x^{v}.

From eq II and IV we predict that the emission yield should continue to increase in this region, Figure 6, but that the emission lifetime should be essentially invariant. Again the experimental and theoretical results are in fairly good agreement. It should be noted that the $1/\tau_{\text{em}}$ scale in Figure 6 is greatly expanded over the corresponding scale in Figure 5. The drop in $1/\tau_{\text{em}}$ in the 0.5-Torr region is associated with the decrease in importance of the diffusional term in eq III at higher pressures. At pressures above 1 Torr it contributes negligibly so that for a constant value of [PhCHO] eq III predicts $1/\tau_{\text{em}}$ is a constant.

(h) **Quenching Constants.** The well-known Stern–Volmer equation for phosphorescence quenching is

$$I(0)/I(\text{Q}) = 1 + \tau_{\text{em}}k_{\text{q}}[\text{Q}] \qquad \text{(V)}$$

where $I(0)$ and $I(\text{Q})$ are the emission intensities in the absence and in the presence of concentration [Q] of quencher and τ_{em} is the lifetime of the emitting state in the absence of quencher. From the data given in Figure 7 together with the lifetime of benzaldehyde at 0.13 Torr from Figure 5 we obtained a k_{q} for DBH $(=k_8)$ of 2.3×10^{10} M^{-1} sec^{-1}. In the same way the k_{q} for AIP was 4.0×10^{10} M^{-1} sec^{-1} while for O_2 the quenching constant was 0.29×10^{10} M^{-1} sec^{-1}. These azo quenching constants are similar to the value already reported[1] for another azo compound DBO, 5.4×10^{10} M^{-1} sec^{-1}, and are close to the collision-controlled value.

(i) **Photolysis of Benzaldehyde in the Presence of DBH.** The results in the previous section show that the interaction constant of DBH with the emitting state of benzaldehyde, T_1^0, is high. The triplet DBH molecules formed by this triplet–triplet transfer have unit probability of dissociation,[1,21] $^3\text{DBH}^* \rightarrow C_5 + N_2$; therefore the C_5 hydrocarbon yield is a convenient measure of the benzaldehyde molecules so trapped. In Figure 8 we have plotted $^{\text{T}}\Phi_{\text{dec}}(C_5)$, the benzaldehyde-sensitized yield of C_5 formation. As the DBH pressure is increased in the range 0–0.25 Torr, $^{\text{T}}\Phi_{\text{dec}}(C_5)$ rapidly increases to a plateau value of 0.63. From eq IV, we calculate that $\Phi_{\text{isc}}(T_1^0)$ at pressures in the range 0.4–0.6 Torr is 0.65. Of course the short-lived T_1^{v} and T_x^{v} molecules which are not trapped by DBH dissociate to form benzene, so we should predict that once the plateau region has been reached, $\Phi_{\text{dec}}(C_6H_6) + {}^{\text{T}}\Phi_{\text{dec}}(C_5) = 1.0$. As can be seen from the first two entries in Table III this is indeed the case. The fact that at DBH pressures which essentially completely quench the phosphorescence, see Figure 7, the benzene yield is ~0.35 is also further indication that benzene can originate from a state other than T_1. At very high pressures, which can be obtained by adding an "inert" gas such as C_2H_6 or CO_2, the T_x^{v} molecules are also deactivated to T_1^0 so the benzene yield should tend to zero while $^{\text{T}}\Phi_{\text{dec}}(C_5)$ should increase from its plateau value of 0.63 and tend to unity. The third and fourth entries in Table III show that this does occur.

(j) **Effect of Temperature.** All the above-mentioned photochemistry was carried out at 22°. We also carried out experiments at 50 and 65°. At both of these temperatures we could observe no significant change in Φ_{em}^{276} or in $\Phi_{\text{dec}}^{276}(C_6H_6)$. At considerably higher temperatures decomposition yields in excess of 40 have been reported.[11]

(5) **Photolysis in the n,π* Region.** (a) **Decomposition and Triplet Yields.** The photochemistry in the

Table III. Quantum Yields in the Photolysis of Benzaldehyde in the Presence of DBH

P_{DBH}, Torr	P_{PhCHO}, Torr	P_M, Torr	λ_{excit}, nm	$\Phi_{dec}(-PhCHO)$	$\Phi_{dec}(C_6H_6)$	$^T\Phi_{dec}(C_5)$
0.261	0.124		276		0.37	0.62
0.294	0.236		276	0.35	0.34	0.62
0.170	0.410	25.4 (C_2H_6)	276		0.05	0.87
0.380	0.350	1500 (CO_2)	276		0.006	0.99
0.090	0.070		284	0.37	0.19	0.66
0.276	0.221		284	0.37	0.19	0.66
0.090	0.070		365	0.42	<0.001	0.73
0.103	0.120		365	0.43	0.0003	0.81
0.192	0.210		365	0.48	0.002	0.83

n,π^* region is quite different from the 276-nm photolysis. The data in Table I show that practically no benzene or CO is formed either for λ_{excit} 328 or 365 nm, although benzaldehyde is consumed with a quantum yield of about 0.4. At the same time we found that on prolonged and repeated photolysis significant amounts of a pale yellow polymeric material built up on the walls of the photolysis vessel. This deposition of polymer on the photolysis of aromatic aldehydes has been observed by other workers,[8-10] indeed De Maré, *et al.*, have used the film as a surface photosensitizer. But only very superficial analyses of the film have been carried out and there is no clear picture as to the route of polymer formation. Blacet and Vanselow[11] have reported finding H_2, benzil, benzophenone, and diphenyl in addition to benzene and carbon monoxide upon radiation of benzaldehyde with 3130-Å light. It is attractive to suggest there are radical-initiated processes. On energetic grounds[28] the most likely candidate is $C_6H_5CHO + h\nu \rightarrow C_6H_5CO\cdot + H\cdot$ since the breaking of the C–C bond, *i.e.*, $C_6H_5CHO + h\nu \rightarrow C_6H_5\cdot + CHO$, should only occur for λ_{excit} <307 nm.[28] Nevertheless it appeared to us that the polymer build-up was more pronounced for the n $\rightarrow$ π^* than for the 276-nm photolysis. In the case of the former the quantum yield of benzaldehyde consumption, $\Phi_{dec}(-PhCHO)$, was unaffected when a triplet scavenger like DBH was added, Table III, indicating that the benzaldehyde consuming process(es) is probably initiated either by radicals originating from S_1 or from a surface initiated reaction.

Benzoin is a product of benzaldehyde irradiation in solution.[29] A CIDNP study[29a] has shown that benzoin formation occurs by the interaction of a triplet and a ground-state benzaldehyde molecule. Hydrogen abstraction results in a radical pair which forms benzoin upon the subsequent combination of this pair. However, benzoin formation *via* the above process cannot be of major importance in the gas phase where the concentrations of benzaldehyde are very low.

In the presence of excess DBH we found that for λ_{excit} 365 nm $^T\Phi_{dec}(C_5) \approx 0.85$. The solution-phase studies by Yang[6,7] involving benzaldehyde indicate a triplet yield of at least 0.75 calculated as the sum of the quantum yields of sensitized isomerization and of oxetane formation in the presence of olefins. It is also interesting to note that in this study it was observed that the quantum yield of oxetane formation was less than the yield of benzaldehyde consumption, indicating the presence of processes other than energy transfer and oxetane formation. If we take $(\Phi_{-PhCHO} - \Phi_{oxet})$ as a measure at these processes, then we have $(\Phi_{-PhCHO} - \Phi_{oxet}) + \Phi_{oxet} + \Phi_{isom} \sim 0.15 + 0.45 + 0.30 = 0.90$. Thus the data indicate that the triplet yield may be less than unity. Based on senisitized isomerization studies in the gas phase De Maré[5b] and coworkers have reported a triplet yield of 1.0. Apparently, however, in the quantum-yield calculations the extinction coefficient at one wavelength was employed although the source was nonmonochromatic, so some small systematic error may have been incurred.

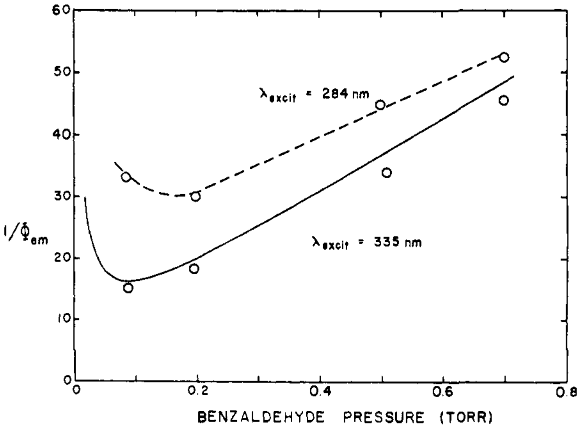


Figure 10. Variation of quantum yield of emission with pressure for λ_{excit} 335 nm and λ_{excit} 284 nm. The solid curve is the model curve for λ_{excit} 335 nm using eq VI and the optimized constants in Table II. The dashed curve drawn through the data for λ_{excit} 284 nm is the best line through the experimental points.

(b) Emission Yields. In terms of the model already presented

$$\Phi_{em}^{n\rightarrow\pi^*} = \Phi_{isc}(T_1^0) \times \frac{k_6}{k_6 + k_7 + k_9[PhCHO] + \{6D/[PhCHO] + 0.81 \times 10^{-7}\}} \quad \text{(VI)}$$

At pressures above 0.2 Torr the diffusional term will be small; therefore, we should have

$$1/\Phi_{em}^{n\rightarrow\pi^*} \approx \frac{k_6 + k_7}{\Phi_{isc}(T_1^0)k_6} + \frac{k_9}{\Phi_{isc}(T_1^0)k_6}[PhCHO]$$

Using the value of $\Phi_{isc}(T_1^0) = k_{13}/(k_{12} + k_{13}) = 0.85$ obtained in the previous section and the value of k_9 given in Table II we can obtain from the slope and intercept of the experimental data given in Figure 10, $k_6 = 4.5 \times 10^2$ sec^{-1} and $k_7 = 2.0 \times 10^3$ sec^{-1}, values which are in fair agreement with the data obtained

---

(28) (a) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, pp 178–215. (b) "Handbook of Chemistry and Physics," 53rd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1972, p F191.

(29) (a) G. L. Closs and D. R. Paulson, *J. Amer. Chem. Soc.*, **92**, 7229 (1970); (b) M. Cocivera and A. M. Trozzolo, *ibid.*, **92**, 1772 (1970).

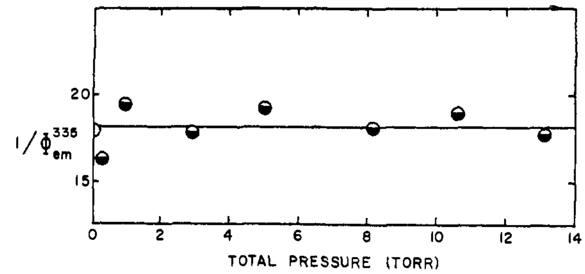


Figure 11. Variation in the phosphorescence yield of benzaldehyde as a function of added ethane λ_{excit} 335 nm: (○) 0.09 Torr of benzaldehyde, (◒) 0.09 Torr of benzaldehyde + C_2H_6 as added gas.

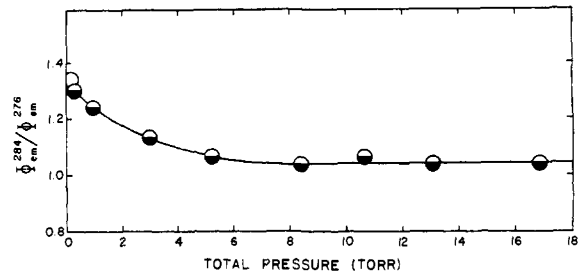


Figure 12. Ratio of emission yields for λ_{excit} 284 nm and λ_{excit} 276 nm as a function of added ethane: (○) 0.2 Torr of benzaldehyde, (◒) 0.2 Torr of benzaldehyde + C_2H_6 as added gas.

for the 276-nm photolysis. The solid curve in Figure 10 is the model curve calculated using eq VI and the data in Table II. It predicts that because of the diffusional terms $\Phi_{em}^{n\rightarrow\pi^*}$ should start to decrease rapidly at pressures below 0.05 Torr. Unfortunately because of the low extinction coefficient of the n → π* band we were not able to carry out measurements in this region with our present apparatus.

The model also predicts that there should be no increase in $\Phi_{em}^{n\rightarrow\pi^*}$ as "inert" gas is added to the system. Figure 11 shows that this is indeed so.

(6) **Photolysis in the 284-nm Region.** Because of the highly structured nature of the absorption in the 284-nm region, absolute quantum yield measurements are subject to greater error than are the 276-nm data. Moreover our studies were much less extensive in this wavelength region. Benzene and CO yields are given in Table I. It will be observed that in the 0–0.2-Torr region the benzene yield drops rapidly to a plateau value of about 0.19. At the same time the data in Table III and Figure 8 show that ${}^{T}\Phi_{dec}(C_5)$ rises to a plateau value of about 0.66; this represents the yield of long-lived trappable triplets. The data indicate then that for λ_{excit} 284 nm $\Phi_{isc}(T_1^v):\Phi_{isc}(T_x^v) = 0.66:0.19$. This may be compared with the ratio 0.68:0.32 for λ_{excit} 276 nm. The selective nature of the exciting wavelength is confirmed in a rather striking way by plotting $\Phi_{em}^{284}/\Phi_{em}^{276}$ as a function of added gas pressure in the 0.2 to 15-Torr range, Figure 12. Although both emission yields increase in this pressure range, Figure 6, the ratio is not constant. In the model we postulated that in this range it is mainly T_x^v molecules which are being deactivated and ultimately feed the emitting triplet. Thus for λ_{excit} 276 nm $\Phi_{isc}(T_1)$ should increase from about 0.68 to 1.0 while for λ_{excit} 284 nm the increase should be from about 0.66 to 0.85. Therefore the relative change in Φ_{em}^{284} should be less than the change for Φ_{em}^{276}.

The data in Table I indicate that for λ_{excit} 284 nm the drop in the benzene yield to the plateau value occurs at lower pressures than does the corresponding drop for λ_{excit} 276 nm. This would imply that the lifetime of T_1^v molecules formed by λ_{excit} 284 nm is greater than that of molecules formed by λ_{excit} 276 nm, which is not surprising since the excess vibrational energy is less for the longer wavelength of excitation. The data in Table III show that $\Phi_{dec}^{284}(C_6H_6) + {}^{T}\Phi_{dec}^{284}(C_5) < 1.0$ and that $\Phi_{dec}^{284}(-\mathrm{PhCHO}) > \Phi_{dec}^{284}(C_6H_6)$. As we have pointed out in the Experimental Section absolute quantum yields for λ_{excit} 284 nm were particularly hard to obtain and it could be that the latter inequality is due to a systematic error. If the difference between benzaldehyde consumption and benzene formation does monitor S_1 reactivity, then the results could indicate that for λ_{excit} 276 nm intersystem crossing is sufficiently rapid to compete favorably with internal conversion, but is somewhat slower in the case of 284-nm photolysis. Theoretical calculations have shown[30] that nonradiative decay rates can be very sensitive functions of energy. Moreover the possibility that there are several triplet states lying close to S_2[17] could also influence the coupling rates.

(7) **General Discussion.** Although in the main the experimental results are rather pleasingly encompassed by the model given in Figure 9 and by eq I–VI, there are certain problems which remain.

We have indicated in section 4c that the experimental evidence points to the existence of a state Γ^v with a lifetime ~10^{-8} sec, which can ultimately be deactivated to the phosphorescing triplet T_1^0. The state Γ^v cannot rapidly interconvert to T_1^v because if this were so there would effectively only be one excited state involved and we should expect no sharp break in the $1/\Phi_{dec}^{276}(C_6H_6)$ *vs.* pressure curve (Figure 3); it would also be hard to explain the increase of Φ_{em}^{276} in the 1–10-Torr region (Figure 6) or the continued formation of benzene in the presence of excess DBH (Table III). We have also presented evidence to show that Γ^v cannot have a large amount of S_0 or S_1 character. But if it is a triplet what state can it be?

It is generally assumed that internal conversion between states occurs much more rapidly than 10^8 sec^{-1}.[22] Thus we have a problem in associating Γ^v with T_2^v, say. If Γ^v were in fact a T_1 state, but with a distribution of the excess vibrational energy differing from that of T_1^v, we should also expect rapid intercommunication between T_1^v and Γ^v.[31] Self-consistent-field MO calculations indicate that there are possibly four ${}^3\pi,\pi^*({}^3L_a)$ states of A′ symmetry lying between $S_2({}^1L_b)$ and $T_1({}^3U)$ which is of A″ symmetry.[17] The symbols in parentheses are often used[35] to describe the different states in aromatic carbonyl compounds. If we consider only the π and n electrons of benzaldehyde, we can represent the electronic structure of T_2 by $(\pi_1)^2(\pi_2)^2(\pi_3)^2(\pi_4)^1(\pi_5^*)^1(n)^2$ and that of T_1 by $(\pi_1)^2(\pi_2)^2(\pi_3)^2(\pi_4)^2(\pi_5^*)^1(n)^1$. It can therefore be seen that the $T_2 \rightsquigarrow T_1$ process involves essentially the transfer of an n electron to the π_4 orbital. Such orbitals are spatially orthogonal and could result in a very low value for the electronic part of the matrix element

---

(30) A. Nitzan, J. Jortner, and P. M. Rentzepis, *Chem. Phys. Lett.*, **8**, 445 (1971).

(31) D. Bunker, *J. Chem. Phys.*, **40**, 1946 (1964).

coupling the states.[22] In this respect it is interesting to note that there are several references in the literature to the involvement of upper triplet states in photochemistry. This could indicate that the upper triplets in these cases do not relax very rapidly to the lowest triplet. One group of compounds where two triplets are apparently involved are lactones and it has been suggested that one triplet has an n,π^* configuration and the other a π,π^* configuration.[32] Also Michl[33] has studied a hydrocarbon in whose photochemistry an upper triplet is involved. It turns out that the molecule has essentially two spatially separate chromophoric groups, the lowest triplet being associated with one and the next triplet with the other. Another possibility which should not be neglected is that Γ is some state in which the nuclear geometry is sufficiently distorted so that it could be regarded as an isomer of benzaldehyde.

For simplicity in Figure 9 we have shown the intersystem crossing for λ_{excit} 276 nm occurring directly from S_2. Operationally this description predicts the observed kinetics; the important fact is that there are two states with very different lifetimes both triplet in character from which benzene is formed. Of course we cannot distinguish between this operational model and other models which have processes too fast for our experiments to detect. Such a process would be internal conversion from S_2 to S_1^{v} before intersystem crossing occurs. However the observations that polymeric build-up seemed to be more severe for $n \rightarrow \pi^*$ photolysis than for $\pi \rightarrow \pi^*$ photolysis and that the polymer apparently originated from S_1 reaction could support the supposition that intersystem crossing competes favorably with internal conversion. Very rapid intersystem crossings have been observed by Rentzepis in the benzophenone system.[30,34] Koyanagi, *et al.*,[35] have experimentally confirmed the intersystem crossing selection rules, $S_1(n,\pi^*) \not\leftrightsquigarrow T_1(n,\pi^*)$ and $S_1(n,\pi^*) \leftrightsquigarrow T_2(\pi,\pi^*)$. If we have two triplets populated, it could mean that there is competition between $S_2(\pi,\pi^*) \leftrightsquigarrow T_1^{\text{v}}(n,\pi^*)$ and $S_2(\pi,\pi^*) \leftrightsquigarrow S_1^{\text{v}}(n,\pi^*)$, with $S_1^{\text{v}}(n,\pi^*)$ finally populating $T_x^{\text{v}}(\pi,\pi^*)$. This would also mean that in the $n \rightarrow \pi^*$ photolysis intersystem crossing from S_1 to T_1, reaction 13 Figure 9, actually occurs *via* T_2.

Harrison and Lossing[36] carried out the Hg-sensitized decomposition of benzaldehyde using light intensities which, judging by the published figures,[1,37] were about one million times greater than ours. Under their conditions the major product was a yellowish polymer but 18% of the yield was C_6H_6 and CO. They found that 67% of the C_6H_6 was formed by a molecular route and 33% by a radical route which they suggested was $C_6H_5CHO^* \rightarrow C_6H_5\cdot + CHO\cdot$ followed by $C_6H_5\cdot + CHO\cdot \rightarrow C_6H_6 + CO$. However in a study of the direct photolysis of benzaldehyde Majer, *et al.*,[16] concluded that all the benzene was formed molecularly. Our results, which show that the quantum yield of benzene formation tends toward unity at low pressure, imply that radical reactions cannot be of major importance since it is unlikely that the fate of every phenyl radical would be benzene. Moreover we have observed that when 0.2 Torr of O_2 was added to 0.7 Torr of benzaldehyde the quantum yield of benzene formation was 0.33 which is close to the value obtained in the absence of oxygen (Table I). Oxygen would be expected to scavenge any radical intermediates very effectively. In the work by Harrison and Lossing[36] it is possible that the increased importance of radical reactions in their system was in part due to the process $Hg(^3P_1) + C_6H_5CHO \rightarrow Hg\text{–}H + C_6H_5CO\cdot$ competing with energy transfer $Hg(^3P_1) + C_6H_5CHO \rightarrow C_6H_5CHO(T) + Hg(^1S_0)$.

For the $S_0 \rightarrow S_2$ band we have discussed the photochemistry resulting from λ_{excit} 276 and 284 nm. In preliminary studies we have found even stronger pressure and wavelength effects for $\lambda_{\text{excit}} < 276$ nm. We have also found that the photochemistry of acetophenone shows many similarities to benzaldehyde (the photochemical and emission yields being strongly influenced by pressure and by the wavelength of excitation). We shall report on these studies later.

Acknowledgment. We are pleased to acknowledge support from the Air Force Office of Scientific Research, Grant 583-66, and from the National Science Foundation, Grant GP-18808.

---

(32) E. Ullman and N. Baumann, *J. Amer. Chem. Soc.*, **92**, 5892 (1970).

(33) J. Michl and J. Kolc, *ibid.*, **92**, 4148 (1970).

(34) P. M. Rentzepis, private communication.

(35) M. Koyanagi, R. Zwarich, and L. Goodman, *Chem. Phys. Lett.*, **9**, 74 (1971).

(36) A. G. Harrison and F. P. Lossing, *Can. J. Chem.*, **37**, 1696 (1959).

(37) F. P. Lossing, D. G. H. Marsden, and J. B. Farmer, *ibid.*, **34**, 701 (1956).