Fe(C$_5$H$_5$)$_2$$^+$] bond, that in HMn(C$_5H_5$)$_2$ may be especially so, perhaps accounting for the fact that the latter species has never been observed while its Tc and Re analogs are well-known. The extension of these results to other organometallic complexes, containing a variety of metal atoms and ligands, should prove illuminating.

References and Notes

(1) Dreyfus Teacher–Scholar, 1971–1976.
(2) For a review of metallocenes, see, for example, M. Rosenblum, "Chemistry of Organometallic Compounds", Wiley-Interscience, New York, N.Y., 1965, Part I.
(3) Previous mass spectral results are summarized in (a) G. M. Begun and R. N. Compton, J. Chem. Phys., **58**, 2271 (1973); (b) R. W. Kiser in "Characterization of Organometallic Compounds", M. Tsutsui, Ed., Wiley-Interscience, New York, N.Y., 1969, Chapter 4; (c) S. Evans, M. L. H. Green, B. Jewitt, A. F. Orchard, and C. F. Pygall, J. Chem. Soc., Faraday Trans. 2, 1847 (1972).
(4) S. M. Schildcrout, J. Am. Chem. Soc., **95**, 3846 (1973).
(5) M. S. Foster and J. L. Beauchamp, J. Am. Chem. Soc., **93**, 4924 (1971); preceding paper in this issue.
(6) For a recent discussion, see D. W. Slocum and C. R. Ernst, Organomet. Chem. Rev., Sect. A, **6**, 337 (1970).
(7) J. L. Beauchamp, Annu. Rev. Phys. Chem., **22**, 517 (1971).
(8) T. B. McMahon and J. L. Beauchamp, Rev. Sci. Instrum., **43**, 509 (1972).
(9) T. B. McMahon, M. S. Foster, and J. L. Beauchamp, to be published.
(10) J. T. S. Andrews and E. F. Westrum, Jr., J. Organomet. Chem., **17**, 349 (1969).
(11) R. J. Blint, T. B. McMahon, and J. L. Beauchamp, J. Am. Chem. Soc., **96**, 1269 (1974).
(12) R. H. Staley and J. L. Beauchamp, J. Am. Chem. Soc., **96**, 6252 (1974).
(13) R. D. Bach, J. Gauglhofer, and L. Kevan, J. Am. Chem. Soc., **94**, 6860 (1972).
(14) G. Gioumousis and D. P. Stevenson, J. Chem. Phys., **29**, 294 (1958).
(15) E. M. Arnett, Acc. Chem. Res., **6**, 404 (1973).
(16) Calculated using ΔH_f°[Fe(C$_5$H$_5$)$_2$] = 51.3 ± 1.3 kcal/mol given in J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970, p 492.
(17) T. J. Curphey, J. O. Santer, M. Rosenblum, and J. H. Richards, J. Am. Chem. Soc., **82**, 5249 (1960).
(18) I. Pavlik and J. Subrt, Collect. Czech. Chem. Comm., **32**, 76 (1967).
(19) J. C. Kotz and D. G. Pedrotty, Organomet. Chem. Rev., Sect. A, **4**, 479 (1969).
(20) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, J. Chem. Soc., 4854 (1961).
(21) M. S. Foster and J. L. Beauchamp, to be published.
(22) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, J. Chem. Soc., 3653 (1962).
(23) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, J. Am. Chem. Soc., **94**, 4728 (1972).
(24) Calculated from eq 10 using IP[Fe(CO)$_5$] = 7.98 eV from G. Distefano, J. Res. Natl. Bur. Stand., Sect. A, **74**, 233 (1970).
(25) R. H. Wyatt, D. Holtz, T. B. McMahon, and J. L. Beauchamp, Inorg. Chem., **13**, 1511 (1974).
(26) F. E. Saalfeld, M. V. McDowell, J. J. DeCorpo, A. D. Berry, and A. G. MacDiarmid, Inorg. Chem., **12**, 48 (1973), and references therein.

Photochemical and Photophysical Processes in Acetophenone

Michael Berger and Colin Steel*

Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154. Received November 25, 1974

Abstract: Besides the first-order radiative (1.2 × 10^2 sec^{-1}) and radiationless (5.3 × 10^2 sec^{-1}) decay channels the lifetime and emission yield of gaseous triplet acetophenone depends upon (a) diffusion to followed by quenching at the wall, (b) self-quenching (8.9 × 10^7 M^{-1} sec^{-1}), and (c) photoreaction. The contribution of diffusion can be treated quantitatively and it is shown that the wall deactivates with close to unit efficiency. At sufficiently low pressure following S$_0$ → S$_2$ excitation, triplet acetophenone dissociates with unit probability to give C$_6$H$_5$CO· + CH$_3$·. The dissociative state can be deactivated by added gas and both emission and chemical quantum yields give a dissociative lifetime of ~5 × 10^{-8} sec for λ_{excit} 275 nm. There is evidence that these lifetimes are wavelength sensitive. S$_0$ → S$_1$ excitation does not result in the above reaction although there is evidence for a temperature-dependent decay.

In a previous paper we discussed the photochemistry of benzaldehyde,[1] and in this paper we report on our studies of acetophenone.[2] Benzaldehyde photochemistry is very sensitive to the energy of excitation and on the nature of the electronic state excited. For example S$_0$ → S$_1$ excitation (n → π*) resulted in free radical formation; S$_0$ → S$_2$ excitation (π → π*) led to an intramolecular process resulting in benzene and CO without the formation of free radicals. The triplet yield was somewhat wavelength dependent, and it has been suggested that the rate of intersystem crossing decreases with an increase in excitation wavelength.[3] Thus we were particularly interested to determine the nature of and the relative importance of the primary photochemical processes in gaseous acetophenone as a function of excitation energy. Furthermore a knowledge of these primary photochemical processes was necessary before studying the bimolecular reactions of triplet acetophenone in the gas phase. The results of these latter studies will be reported in another paper.[4]

Early studies[5,6] of the photolysis of acetophenone were directed to the search for a convenient source of phenyl radicals in the gas phase. Both methyl and phenyl radicals were produced in sufficient quantity for rate studies when photolyses using an unfiltered mercury arc were carried out at elevated temperatures (>280°).[6] Carbon monoxide, benzene, ethane, methane, and trace amounts of biphenyl and toluene were produced under these conditions. The use of acetophenone as a radical source in the glass was also attempted.[7] However, full mercury arc irradiation of acetophenone in a 5:1 isopentane-3-methylpentane glass at liquid nitrogen temperature resulted in no detectable decomposition.

The above mentioned studies reveal little about the nature of the primary photochemical processes involved since unfiltered light was used. Smith and Calvert[8] studied the S$_0$ → S$_1$ photolysis of trifluoroacetophenone at 366 and 313 nm at elevated temperatures (150-300°). They concluded the quantum yield for decomposition was extremely small, under their conditions: for example, at 366 nm and 280°, Φ_{CF_3} ~ 0.008.

Experimental Section

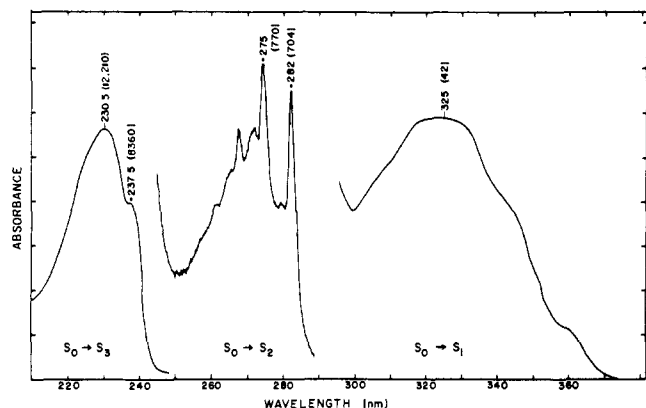(1) **Materials and Apparatus.** Acetophenone was distilled on a

Figure 1. Gas-phase absorption spectrum of acetophenone in the 210–380 nm range. The region 210–290 nm was recorded at 0.4 Torr (25°) and the n,π* region at 4.6 Torr (65°). The extinction coefficients in M^{-1} cm^{-1} are given in parentheses along with peak maxima.

micro Vigreux column at reduced pressure and then further purified by 4–5 trap distillations under vacuum immediately before use. Carbon dioxide was used as an "inert gas" in some experiments; it was also vacuum distilled immediately before use. Carbon dioxide was employed because it was chemically inert, there being no abstractable hydrogens,[9] and because it could be readily degassed to remove trace amounts of oxygen. Even small concentrations of the latter can quench the triplet.[1] Benzene, toluene, methane, and ethane were similarly purified for gas chromatographic calibrations.

General descriptions of the photolysis, the emission, and the lifetime equipment have already been given.[10,11] The methods used to determine decomposition and emission quantum yields are also found in these references. For emission measurements rectangular 1 cm path length quartz (Suprasil) fluorescence cells were used. For lifetime measurements, at very low pressures of acetophenone the emission signal was shot-noise limited when the above quartz cells were used. Thus a special cylindrical cell 6 cm in diameter and 3 cm high fabricated from aluminum and anodized black was constructed to increase the amount of light exciting the gas. A 3 cm square quartz excitation window was epoxied into the bottom of the cell and a 0.5 × 1.5 cm quartz window was inset into the side of the cell to monitor the emission. This cell could be situated less than 1 cm from the excitation source. With this setup the signal level was increased more than 200-fold and the relative scatter was decreased substantially. Lifetimes of 3 × 10⁻³ Torr of acetophenone could be reproducibly obtained. Another advantage of this large cell is that effects of diffusion to the wall are minimized.

For lifetime measurements at elevated temperatures, the rectangular quartz cells were placed in a 6.5 × 6.5 × 10 cm brass block equipped with appropriate excitation and emission windows. The block, heated by cartridge heater elements, could be held to within 0.1° as measured by a thermocouple in contract with the quartz cell.

Photolyses were carried out at room temperature, 22 ± 2°, using a high-pressure mercury arc (PEK 100 W)/Bausch and Lomb monochromator combination with an effective spectral bandwidth of 6.6 nm. The cylindrical quartz photolysis cells were 17 cm in length with a diameter of 3 cm. Analysis for gaseous products was carried out by gas chromatography using flame ionization and thermal conductivity detectors. The extent of photolysis was generally less than 15%. It should be pointed out that the strong absorptive nature of gaseous acetophenone in the vacuum system necessitated special care to ensure equilibrium when preparing samples.[1]

(2) Spectra. The gas phase absorption spectrum of acetophenone is shown in Figure 1. The peak maxima and the corresponding extinction coefficients are given on the spectrum. It should be pointed out that because of the narrowness of the 275 and 282 nm peaks, a special bandwidth of less than 0.4 nm had to be employed in order to obtain correct extinction coefficients in these regions. Extinction coefficients and acetophenone vapor pressures were determined simultaneously using a spectrophotometric method.[12] The vapor pressure fits the following expression in the range 0–103°: log $P_{Torr} = B - [.2185A/(T + 273)]$. Experimentally, we find $A =$
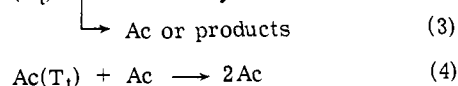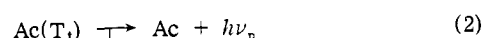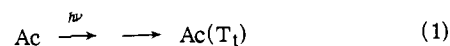
11,800 (the heat of vaporization in cal/mol) and $B = 8.3$. This agrees excellently with the literature[13] values $A = 11,732$ and $B = 8.233$ over the temperature range 37–202°.

Using a 4 nm spectral bandwidth the gas emission spectrum at room temperature had major peak maxima at 392, 420, and 450 nm with corrected relative intensities of 0.66:1.00:0.84. The spectrum is quite similar to that obtained in isooctane at room temperature, viz., 394, 421, and 451 nm.[14] In a hydrocarbon glass at 77°K with 1 nm dispersion the spectrum sharpens up considerably and the 0–0 maximum shifts to 389 nm in agreement with other studies.[15,16] Emission quantum yield studies as a function of wavelength were carried out using a 4 nm spectral bandwidth for the excitation monochromator and a 20 nm pass for the emission monochromator.

Results and Discussion

(1) Emission and Lifetime Studies. (a) $S_0 \rightarrow S_1$ Excitation. (i) Diffusion and Self-Quenching Effects. One of the problems in measuring triplet lifetimes and emission yields results from diffusion of excited molecules to the vessel wall where they are effectively quenched. In the following model we take diffusion into account in order to explain the behavior of acetophenone (Ac) at very low pressures.

$$Ac \xrightarrow{h\nu} \longrightarrow Ac(T_t) \qquad (1)$$

$$Ac(T_t) \begin{array}{c} \longrightarrow Ac + h\nu_p \\ \longrightarrow Ac \text{ or products} \end{array} \begin{array}{c} (2) \\ (3) \end{array}$$

$$Ac(T_t) + Ac \longrightarrow 2Ac \qquad (4)$$

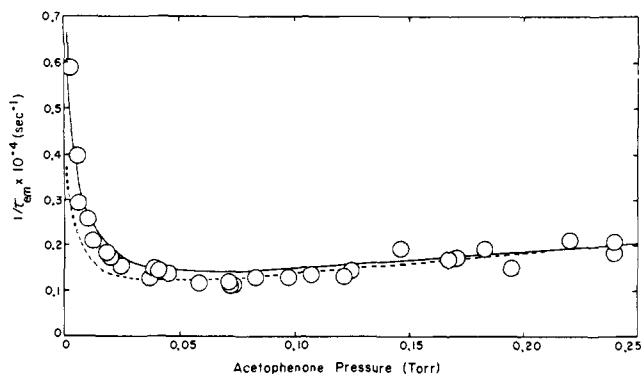$$Ac(T_t) \xrightarrow{wall} Ac \qquad (5)$$

Reaction 1 includes absorption and intersystem crossing. Since these are so rapid compared with the decay channels the value of k_1 does not enter into the subsequent kinetic expressions.

Processes 2 and 3 represent the radiative and first-order nonradiative decay channels. Reaction 4 is the self-quenching reaction which has been observed both in the gas phase and for solution.[4,9,17,18] Reaction 5 is diffusion to the wall followed by deactivation. At 3 × 10⁻³ Torr, the lowest pressure employed in the lifetime studies, the mean free path of acetophenone molecules, is ∼0.4 cm which is comparable with the dimensions of the vessel employed (see Experimental Section). Assuming that the exciting flash fills the vessel uniformly the excited molecules have to travel in the collision free region an average distance $(\sigma) = 2$ cm to reach the wall. The time (t_0) required to travel such a distance is 80 μsec. The smallest actual lifetime measured was 170 μsec, so that in the collision-free region the lifetime would be ≲170 μsec. Thus we estimate a wall accommodation coefficient $(\alpha) \gtrsim 80/170 \sim 0.5$.

At higher pressures of acetophenone the time to reach the wall is limited by diffusion. This time is given by $t_{diff} \sim \sigma^2/6 \mathfrak{D} = \sigma^2[Ac]/6D$. $\mathfrak{D}$, the diffusion coefficient, and D can be calculated from standard formulas.[19] This means that over the whole pressure range the time to reach the wall and be quenched can be given approximately by $t_{wall} \sim \{(\sigma^2[Ac]/6D) + t_0\}(1/\alpha)$. Thus the measured emission lifetime becomes

$$\frac{1}{\tau_{em}} = \{k_2 + k_3\} + k_4[Ac] + \alpha \left\{ \frac{\sigma^2[Ac]}{6D} + t_0 \right\}^{-1}$$

(I)

For a molecular diameter of 8 Å we estimate $D = 7.9 \times 10^{-4} M$ cm² sec⁻¹ at 25°. At pressures above 0.05 Torr (2.7 × 10⁻⁶ M) the third term becomes small so $\{k_2 + k_3\}$ and k_4 can be estimated from the "straight-line" portion of the curve; see Figure 2. These quantities were found to have the

Figure 2. Variation in the reciprocal of the acetophenone triplet lifetime. τ_{em}, with acetophenone pressure: (O) experimental values; — and - - - calculated from eq 1 using $\alpha = 1.0$ and 0.5, respectively.

values 800 sec^{-1} and 8.8×10^7 M^{-1} sec^{-1}, respectively. The full-line curve in Figure 2 was obtained using these values and setting $\alpha = 1.0$; the dashed curve was obtained using $\alpha = 0.5$. By forcing the data above 0.05 Torr to fit a straight line too high an intercept is obtained because there is significant upward curvature in the 0.05–0.15 Torr range due to diffusion. In fact an even better fit to the data is obtained with $\alpha = 1.0$, $k_4 = 8.9 \times 10^7$ M^{-1} sec^{-1}, and $(k_2 + k_3) = 650$ sec^{-1}.
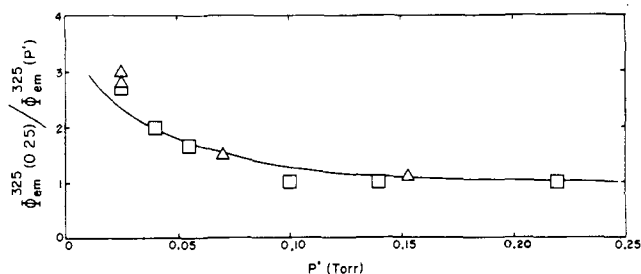
(ii) Quantum Yields. The decrease in lifetime due to diffusion of triplets to the wall should also be reflected in a drop in the emission yield since

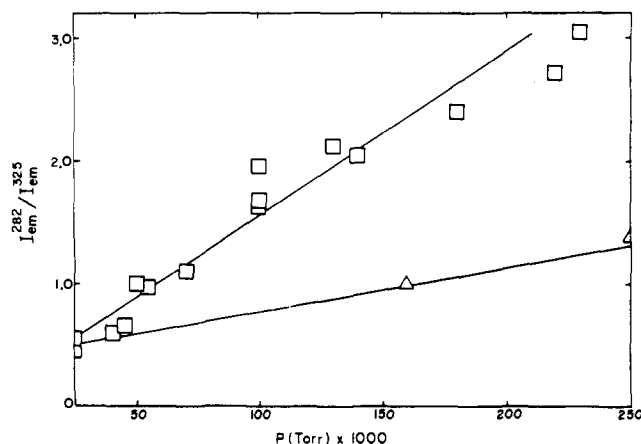$$1/\tau_{em} = k_2/\Phi_{em} \qquad (\text{II})$$

These yields were determined using a rectangular 1 cm path length quartz cell. The data are shown in Figure 3. The full-line curve was calculated using eqs I and II. Because of the smaller dimensions of this cell in comparison to the vessel employed in the previous section, diffusional effects are more significant. It will be noted that in this case the diffusional effect masks the self-quenching, i.e., the $k_4[Ac]$ term does not contribute significantly in this pressure regime in the smaller vessel. Simple theory shows that acetophenone should diffuse through CO_2 three times faster than through itself. It is for this reason that when CO_2 was present as an added gas we set its efficiency β in impeding diffusion to the wall as $\frac{1}{3}$ that of acetophenone, i.e., $t_{diff} \approx (\sigma^2/6D)\{[Ac] + \beta[CO_2]\}$.

(iii) Radiative Lifetimes. Both the quantum yields and lifetimes were sensitive to the purity of acetophenone. In the 1 cm fluorescence cell with enough CO_2 added (~ 60 Torr) to minimize diffusional effects we could obtain lifetimes as long as 500 μsec ($P_{Ac} = 0.25$ Torr) and as short as 300 μsec with a "poor" sample with corresponding variations in Φ_{em}. With an observed lifetime of 500 μsec, $\Phi_{em} = 0.06$. This gives a radiative lifetime of 8.3 msec in good agreement with the values obtained in the glass and in solution.[14,15,20] Thus $k_2 = 1.2 \times 10^2$ sec^{-1} so that $k_3 = 5.3 \times 10^2$ sec^{-1}. Our value of $k_2/(k_2 + k_3) = 0.18$ can be compared with 0.62 in the glass. The difference may reflect small variations in k_2 and/or k_3 with phase or temperature.
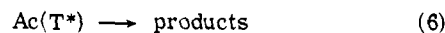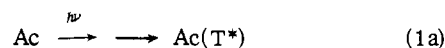
(b) $S_0 \rightarrow S_2$ Excitation. Effect of Pressure on Emission Yields. Although little photochemistry results from $S_0 \rightarrow S_1$ excitation at room temperature, extensive decomposition does occur upon excitation in the S_2 band at low pressures (vide infra). In the scheme below reaction 1a represents $S_0 \rightarrow S_2$ excitation followed by intersystem crossing to produce a vibronically excited triplet. Decomposition (reaction 6) or collisional deactivation (reaction 7), are the two fates of this triplet.

Figure 3. Relative emission quantum yields as a function of effective pressure, P', for λ_{excit} 325 nm ($P' = P_{Ac} + 0.33P_{CO_2}$): (□) acetophenone alone. (△) CO_2 as added gas. $P_{Ac} = 0.025$ Torr. Full-line calculated using eqs 1 and 11 with $\sigma = 0.4$ cm and $\alpha = 1.0$.

Figure 4. Ratio of emission intensities for λ_{excit} 282 and 325 nm as a function of presssssure ($P = P_{Ac} + P_{CO_2}$): (□) acetophenone alone, (△) CO_2 as added gas. $P_{Ac} = 0.025$ Torr. The emission intensities are corrected such that the excitation intensity is independent of wavelength.
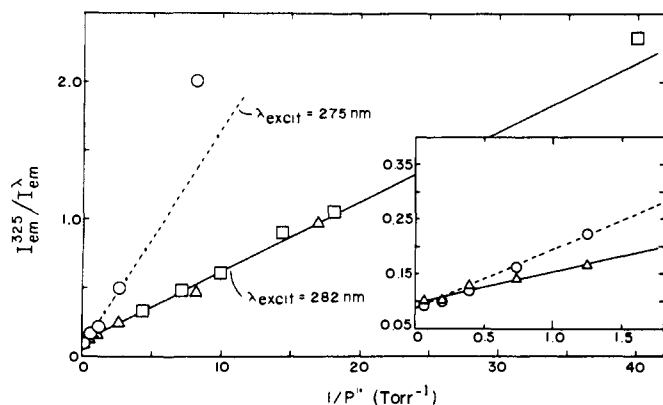
$$Ac \xrightarrow{h\nu} \longrightarrow Ac(T^*) \qquad (1a)$$

$$Ac(T^*) \longrightarrow products \qquad (6)$$

$$\xrightarrow{+M} Ac(T_1) \qquad (7)$$

$Ac(T_1)$ can then carry out reactions 2–5, discussed previously. The efficiency of CO_2 relative to ground-state acetophenone as a deactivating agent, reaction 7, was determined by measuring the emission intensity for λ_{excit} 282 nm relative to the emission intensity for λ_{excit} 325 nm as a function of pressure, Figure 4. Such relative measurements have the advantage that diffusional effects will cancel. The data in Figure 4 show that CO_2 is about one quarter as effective as ground-state acetophenone in removing excess energy from excited triplet acetophenone, $Ac(T^*)$. In terms of the above model

$$\Phi_{em}{}^\lambda = \frac{k_7[M]}{k_6{}^\lambda + k_7[M]} \Phi_{em}{}^{325} \qquad (\text{III})$$

This predicts that at sufficiently high pressures, $\Phi_{em}{}^\lambda$ becomes equal to $\Phi_{em}{}^{325}$. Equation 111 can be rearranged to

$$\frac{I_{em}{}^{325}}{I_{em}{}^\lambda} = \frac{\epsilon^{325}}{\epsilon^\lambda}\left\{1 + \frac{k_6{}^\lambda}{k_7[M]}\right\} \qquad (\text{IV})$$

In eq IV $I_{em}{}^{325}$ and $I_{em}{}^\lambda$ are the experimental emission intensities at $\lambda_{excit} = 325$ nm and $\lambda_{excit} = \lambda$, corrected such that the excitation intensity is independent of wavelength. It is also assumed that absorbances are small enough to write $I_{abs}{}^{325}/I_{abs}{}^\lambda = \epsilon^{325}/\epsilon^\lambda$, the ratio of the effective extinction coefficients for the spectral bandwidth of the exciting radia-

Figure 5. Ratios of emission intensities for λ_{excit} 274 and 282 nm vs. λ_{excit} 325 nm as a function of effective pressure P'' ($P'' = P_{Ac} + 0.25P_{CO_2}$): (□) acetophenone alone, λ_{excit} 282 nm; (△ and ○) CO_2 as added gas. $P_{Ac} = 0.025$ Torr and λ_{excit} 282 and 275 nm, respectively. Insert: data in high-pressure region with same variables on expanded scales. The emission intensities are corrected such that the excitation intensity is independent of wavelength.

Figure 6. Quantum yield of ethane formation as a function of effective pressure P'' for λ_{excit} 275 nm where $P'' = P_{Ac} + 0.25P_{CO_2}$.

tion, which in this case was 4 nm. If the model is correct, the intercepts in Figure 5 should equal 0.089 and 0.071, the experimental values of $\epsilon^{325}/\epsilon^\lambda$ obtained from the absorption spectra for λ 282 and 275 nm, respectively, using a 4 nm band pass. The actual intercepts obtained from Figure 5 were 0.095 ± 0.01 and 0.08 ± 0.01. The good agreement indicates that at high pressures Φ_{em}^{282} and Φ_{em}^{275} do indeed approach Φ_{em}^{325}. Returning to eq IV and Figure 5 we find from the slope that $k_6^\lambda = 2.5 \times 10^7$ and 1.3×10^7 sec^{-1} for λ 275 and 282 nm, assuming k_7 has the collision controlled value 3.9×10^{11} M^{-1} sec^{-1} for M = acetophenone.
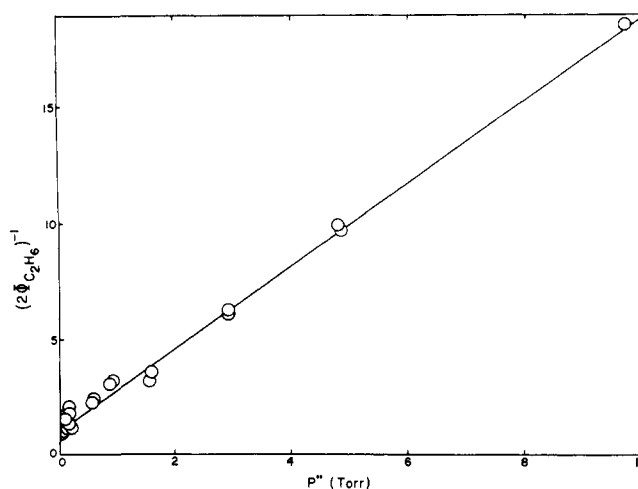
(c) $S_0 \rightarrow S_3$ Excitation. At the highest pressures employed, ~60 Torr CO_2, emission resulting from λ_{excit} 230 and 238 nm could be observed. Extensive measurements for this band have not been carried out yet but $\Phi_{em}^{230} \ll \Phi_{em}^{275}$ at 60 Torr so that considerably higher pressures are required to deactivate the molecules excited into S_3.

Acetophenone was incorporated into a 2-methylbutane glass and the quantum yields of emission were determined for λ_{exit} ranging from 230 to 340 nm. Within experimental error the quantum yield remained constant indicating a constant emission yield for excitation into the S_1, S_2, and S_3 bands, which is consistent with the absence of photochemistry in the glass.[7] Of course this constancy could stem from relaxation in the singlet before intersystem crossing but if the latter can compete with the former, at sufficiently high pressures the highly excited triplets must be deactivated efficiently. These results are similar to those of Metcalfe et al.[3] who observed that the quantum yield of emission for benzaldehyde was also pressure sensitive for λ_{excit} 230 nm.

(2) Photochemistry. (a) $S_0 \rightarrow S_2$ Excitation. When 0.2 Torr of acetophenone was photolyzed at 275 nm at room temperature ethane was the major gaseous product. It was shown that the amount of ethane produced was a linear function of the total quanta absorbed up to 25% decomposition. However, in general, photolyses were carried out to less than 15% decomposition to minimize complications from side reactions. Moreover it was demonstrated that $\Phi(-Ac) = 2\Phi(C_2H_6)$; this latter result indicates that the major photochemical channel is

$$Ac \xrightarrow{h\nu} C_6H_5CO + \cdot CH_3 \qquad (6a)$$

At the lowest pressures used the efficiency of the recombination of methyl radicals to form ethane is reduced because of subsequent dissociation of some of the $C_2H_6^*$,[21] but the

absence of other channels for methyl radicals in our system ensures that C_2H_6 is the ultimate product. Reaction 6a is expected on simple energetic grounds since the reactions of acetophenone to form ($C_6H_5\cdot + CH_3CO\cdot$) and ($C_6H_5CO\cdot + CH_3\cdot$) are endothermic by 93.8 and 80.7 kcal, respectively.[22,23] Since we could detect no carbon monoxide, $[C_2H_6]/[CO] > 100$, the $C_6H_5CO\cdot$ radical does not decompose under our conditions, but may be expected to do so at higher temperatures since its activation energy for decomposition is known to be 29.2 kcal mol^{-1}.[22] A typical hydrocarbon analysis gave ethane:benzene:methane:toluene = 1.0:0.02:0.006:0.002. As has been generally found in the gas phase photolysis of aromatic carbonyls, on prolonged irradiation the buildup of pale yellow "polymeric" layer on the vessel walls could be observed. This material on extraction with acetonitrile was shown to have a long structureless absorption extending beyond 400 nm with a distinct peak at 243 nm. Thin-layer chromatography indicated that neither biphenyl nor benzil was major component of this material.

Since reaction 6a seems to be the major photochemical channel the model predicts

$$1/2\Phi_{C_2H_6} = 1 + k_7[M]/k_6 \qquad (IV)$$

The pressure dependence of the ethane quantum yield is shown in Figure 6. Using the value for k_7 and the deactivation efficiencies for acetophenone and carbon dioxide calculated above we obtained $k_6^{275} = 1.4 \times 10^7$ sec^{-1}. Although this value is close to that obtained from the emission studies $(2.5 \times 10^7 \text{ sec}^{-1})$, it does differ by almost a factor of 2. At present we are not able to explain this disrepancy.

A few photolyses at 282 nm and at 250 nm were also carried out. The results were very much like the 275 nm photolyses, high quantum yields of decomposition at low pressures with similar product distributions.

It may be asked why we have concluded that for $S_0 \rightarrow S_2$ excitation decomposition occurs from the triplet rather than from, say, S_1^{vib}. The same reasoning as was used previously can be applied. The lifetime of the dissociative state is ~10^{-7} sec. The radiative lifetime of S_1 is ~10^{-6} sec, so that if S_1 lived for as long as 10^{-7} sec we would expect to see strong fluorescence. Furthermore all the evidence points to the intersystem crossing rate in aromatic carbonyls as being very much greater than 10^7 sec^{-1}.[24]

(b) $S_0 \rightarrow S_1$ Excitation. The use of 365 nm radiation allows excitation close to the onset of the $S_0 \sim S_1$ transition. Very low quantum yields of methane and ethane formation were obtained, even at low acetophenone pressures, for
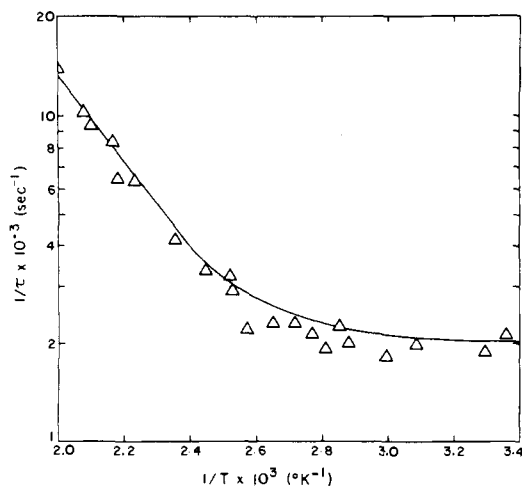
Figure 7. Variation in acetophenone triplet lifetime (τ) with temperature. Acetophenone (0.2 Torr) with 60 Torr of CO_2 as added gas.

room temperature photolyses. This result is in good agreement with the $S_0 \rightarrow S_1$ photolyses of trifluoroacetophenone where low quantum yields of decomposition were reported. We estimate $\Phi_{CH_3} < 0.01$ from our data. Thus decomposition from T_1 into products represents a very small fraction of reaction 3. Methane was the major product; $(CH_4)/(C_2H_6) = 2.2$. The larger relative amount of methane to ethane in $S_0 \rightarrow S_1$ photolyses compared with that in the $S_0 \rightarrow S_2$ photolyses presumably stems from the much lower steady state methyl radical concentration in the $S_0 \rightarrow S_1$ photolyses. Thus we conclude that the quantum yield of channel 6a is much smaller for $S_0 \rightarrow S_1$ excitation than for $S_0 \rightarrow S_2$ excitation.

A recent study of gaseous benzophenone demonstrated that the observed lifetime of triplets produced by $S_0 \rightarrow S_1$ excitation varied markedly with temperature.[25] This effect had also been observed in solid matrices[26] and there was evidence that it was caused by a temperature-dependent chemical channel. Preliminary data indicate that similar effects might be operating for both benzaldehyde and acetophenone. Figure 7 is a plot of triplet acetophenone lifetime vs. temperature. Over a considerable range of temperature the lifetimes remain essentially constant, but decrease markedly at higher temperature.

The full line in Figure 7 has been calculated by fitting the data to the sum of temperature-dependent, k_T, and temperature-independent, k_0, rate constants: $k_{obsd} = k_0 + k_T = 2.0 \times 10^3 + 10^{7.8} e^{-8600/RT}$. The temperature-dependent process could be a chemical channel and may explain the steadily increasing CF_3· yield observed by Smith and Calvert as they increased the temperature in the photolysis of trifluoroacetophenone.

The variation in the lifetime due to the temperature dependence of self-quenching in gaseous acetophenone has been studied and has been shown to be too small to explain the results in Figure 7. The self-quenching process is discussed more fully in a forthcoming paper dealing with bimolecular reactions of triplet acetophenone.

Conclusions

The primary photophysical and photochemical processes in benzaldehyde and acetophenone have certain striking similarities and differences. In both cases the triplet molecules are readily quenched with almost unit efficiency on the walls of the reaction vessel; this can become the dominant decay route at low pressures. Self-quenching is also important in both cases. The photochemical yields are markedly wavelength and pressure sensitive with chemical quantum yields and emission yields correlating in a pleasing fashion. However, the major photochemical reactions, which can occur with high quantum yield under the appropriate conditions, are quite different in booth cases. Benzaldehyde yields benzene and carbon monoxide while for acetophenone the major pathway is the production of C_6H_5CO· and CH_3·. The onset wavelengths of the photochemical channels and their general natures are strikingly confirmed by the opto-acoustic spectroscopy technique.[27]

Both benzaldehyde and acetophenone promise to be interesting systems for study in the isolated molecule region. However, more detailed studies over wider ranges of excitation wavelength, pressure, and temperature are required to reveal whether there is more than one photochemical channel in each case and whether decompositions can be treated simply in terms of the unimolecular reaction of a vibrationally excited triplet or if there are more subtle matchings at particular energies with dissociative surfaces.

References and Notes

(1) M. Berger, I. L. Goldblatt, and C. Steel, *J. Am. Chem. Soc.*, **95**, 1717 (1973).
(2) A preliminary account of this work was reported by C. Steel, Abstracts, Third International Symposium on Gas Kinetics, Brussels, Belgium, August 1973.
(3) J. Metcalfe, R. G. Brown, and D. Phillips, to be published.
(4) Preliminary results have been presented by J. A. Bell, M. Berger, L. Giering, and C. Steel, Abstracts, 11th Informal Conference on Photochemistry, Vanderbilt University, Nashville, Tenn., June 16–20, 1974.
(5) H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, 589 (1939).
(6) F. J. Duncan and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4672 (1962).
(7) R. G. Snowden and N. Davidson, *J. Am. Chem. Soc.*, **78**, 1291 (1956).
(8) R. M. Smith and J. G. Calvert, *J. Am. Chem. Soc.*, **78**, 2345 (1956).
(9) L. Giering, M. Berger, and C. Steel, *J. Am. Chem. Soc.*, **96**, 953 (1974).
(10) W. Clark and C. Steel, *J. Am. Chem. Soc.*, **93**, 6347 (1971).
(11) B. Soloman, T. Thomas, and C. Steel, *J. Am. Chem. Soc.*, **90**, 2249 (1968).
(12) M. Berger, J. A. Bell, and C. Steel, *J. Chem. Educ.*, **52**, 191 (1975).
(13) "Handbook of Chemistry and Physics", 51st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1970, p D 146.
(14) W. D. K. Clark, A. D. Litt, and C. Steel, *J. Am. Chem. Soc.*, **91**, 5413 (1969).
(15) J. B. Gallivan, *Can. J. Chem.*, **50**, 3601 (1972).
(16) Y. H. Li and E. C. Lim, *Chem. Phys. Lett.*, **7**, 15 (1970).
(17) C. A. Parker and T. A. Joyce, *Trans. Faraday Soc.*, **65**, 2823 (1968).
(18) L. Giering, Ph..D. Thesis, Brandeis University, 1974.
(19) W. Kauzmann, "Kinetic Theory of Gases", W. A. Benjamin, New York, N.Y. 1966, p 204.
(20) D. R. Kearns and W. A. Case, *J. Am. Chem. Soc.*, **88**, 5087 (1966).
(21) E. V. Waage and B. D. Rabinovitch, *Int. J. Chem. Kinet.*, **3**, 105 (1971).
(22) R. K. Solly and S. W. Benson, *J. Am. Chem. Soc.*, **93**, 2127 (1971); S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.
(23) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London, 1970.
(24) R. M. Hochstrasser, H. Lutz, and G. W. Scott, *Chem. Phys. Lett.*, **24**, 162 (1974).
(25) J. A. Bell, M. Berger, and C. Steel, *Chem. Phys. Lett.*, **28**, 205 (1974).
(26) P. F. Jones and A. R. Calloway, *Chem. Phys. Lett.*, **10**, 438 (1971).
(27) M. B. Robin and N. A. Kuebler, *J. Am. Chem. Soc.*, following paper in this issue.