Electronic Relaxation Processes in Acetone and 1,1,1-Trifluoroacetone Vapor and the Gas Phase Recombination of the Acetyl Radical at 22 °C

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Abstract: The photochemistry and photophysics of acetone and 1,1,1-trifluoroacetone excited in the $\pi^* \leftarrow n$ transition have been reinvestigated at various excitation wavelengths (330–250 nm), pressures (0–1000 Torr), and rates of light absorption at room temperature. Quantum yields of phosphorescence, intersystem crossing, biacetyl production, and carbon monoxide production were measured. Biacetyl production was monitored by detecting its sensitized phosphorescence while CO production was followed by monitoring its $A(^1\pi) \rightarrow X(^1\Sigma^+)$ resonance fluorescence. At sufficiently high light intensity, product quantum yields became independent of light intensity and gave evidence for two modes of primary photodissociation; their relative importance as a function of excitation wavelength was studied. The limiting values of biacetyl yield at high intensity deviated considerably from that predicted by simple collision theory and may be interpreted as evidence that acetyl radicals may recombine along triplet and singlet potential surfaces. At lower light intensities, the parametric dependence of the quantum yield of biacetyl production gave quantitative information on the rate of acetyl radical decomposition. This rate constant was found to be independent of excitation wavelength but was pressure dependent. The dependence of the lifetimes of excited states preceding decomposition on the excitation wavelength was investigated by measuring the pressure dependence of the quantum yield of intersystem crossing. No evidence for excited states with lifetime intermediate between those of the excited singlet and thermalized triplet was found. Two mechanisms can account for this observation: the excited singlet state is more effectively depleted at higher internal energies by a nonradiative process other than intersystem crossing, and/or, triplet state molecules with energies above a certain minimum value have lifetimes shorter than those measured for the singlet state. Evidence is advanced in favor of the second explanation.

During a recent study of the phosphorescence of 1,1,1-trifluoroacetone[1] we noticed that the intensity of emitted light increased with time; this effect is due to the accumulation of the photolysis product, biacetyl, in the system and the subsequent sensitization of its triplet emission by 1,1,1-trifluoroacetone. We found moreover that this effect allowed us to detect in a routine manner extremely small quantities of biacetyl in the system (less than 1.0×10^{-5} Torr)[2] and consequently we were able to measure small rates of production (less than 5×10^{-16} mol cm^{-3} s^{-1}) of this compound. We note at this point that this technique of monitoring biacetyl production was first used by Heicklen and Noyes[3] who applied it to a limited extent in a study of the 313-nm photolysis of acetone at 40 °C. We have used it to study the room-temperature photolysis of acetone and 1,1,1-trifluoroacetone at various excitation wavelengths (340–240 nm) and in the presence of various pressures of inert gas (0–900 Torr of carbon dioxide). The results contribute to the understanding of the primary photophysics and photochemistry of these molecules and to the secondary reactions of the acetyl radical. In order to highlight the areas of relevance of these results it is convenient to present a short summary of the existing literature on the photochemistry of these two molecules.

The literature on the photochemistry of acetone is extensive and thorough and has been previously reviewed.[4,5] The most generally accepted reaction mechanism for the formation of products is due to Noyes and Dorfman:[6]

$$CH_3COCH_3^* \rightarrow 2CH_3 + CO \qquad k_1 \qquad (1)$$

$$CH_3COCH_3^* \rightarrow CH_3CO + CO \qquad k_2 \qquad (2)$$

$$CH_3CO \rightarrow CH_3 + CO \qquad k_3 \qquad (3)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad k_4 \qquad (4)$$

$$CH_3 + CH_3CO \rightarrow CH_3COCH_3 \qquad k_5 \qquad (5)$$

$$CH_3CO + CH_3CO \rightarrow CH_3COCOCH_3 \qquad k_6 \qquad (6)$$

$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3 \qquad k_7 \qquad (7)$$

There are however several points of disagreement in the literature concerning this mechanism. Thus Noyes and Dorfman[6] found values of α $(=k_1/(k_1 + k_2))$ of 0.07 and 0.22 at 313 and 254 nm, while Martin and Sutton[7] found $\alpha = 0$ at 313 nm and concluded it likely that $\alpha = 0$ at 254 nm. O'Neal and Benson confirmed that $\alpha = 0$ at 313 nm.[8] There is also disagreement as to the secondary reactions, some groups considering the formation of biacetyl to be in part a wall reaction[9-11] while others regard it as a homogenous gas phase recombination.[8] Calvert[12] has noted that this dichotomy has led to different interpretations of the unimolecular decomposition of the acetyl radical. Some authors have considered it in its high pressure limit at normal pressures[6,13] while others have placed it in a pressure-dependent regime.[8,14-17]

The question, which excited states of acetone lead to the primary dissociative acts, was first investigated by Heicklen and Noyes who showed that part of the photodecomposition was quenched by biacetyl formed during the photolysis.[3,18] This aspect of the photolysis has been extensively investigated by Cundall and Davies[19] and by Larson and O'Neal.[20,21] The former authors proposed a triplet state decomposition, $k_2^t = 2.5 \times 10^{10} \exp(-6400/RT)$ s^{-1}, and a singlet state decomposition, $k_2^s = 2.5 \times 10^{16} \exp(-16900/RT)$ s^{-1}, and found no pressure dependence for the triplet state decomposition.[19] The latter authors concluded that all photodecomposition takes place from the triplet manifold in one (or both) of two ways: by a unimolecular pressure-dependent thermal decomposition of the low-lying energy levels of the triplet and by a spontaneous decomposition from upper vibrational levels of the triplet.[21] A value for the activation energy of triplet state decomposition of 10 ± 1 kcal mol^{-1} was found. The pressure dependence of the unimolecular decomposition was inferred from the pressure dependence of the phosphorescence lifetime [$\tau_p^{-1} = b + cP/(1 + dP)$, where P is acetone pressure] found by Kaskan and Duncan.[22]

It has been proposed that internal conversion to vibrationally excited ground states should play a dominant role in aliphatic ketone photochemistry.[23] None of the above studies have considered this possibility in assigning intimate pathways for

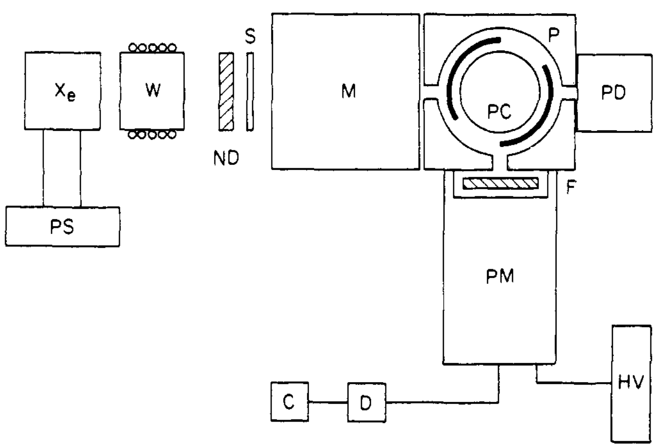


Figure 1. Apparatus to measure quantum yield of biacetyl production: PS, Hewlett-Packard 6269B power supply; Xe, 1000W xenon arc lamp; W, water-cooled water filter; ND, neutral density filter; S, shutter; M, Schoeffel GM250 0.25 m monochromator; P, thermostated, rotating can phosphorimeter; PC, 4 cm diameter, 60 cm^3 volume, Suprasil A phosphorimeter cell; PD, RCA 935 photodiode; F, Corning CS 0-51 glass filter; PM, EMI 6256 photomultiplier; HV, Fluke 412B power supply; D, Ortec 463 100 MHz discriminator; C, Ortec 720 counter/timer.

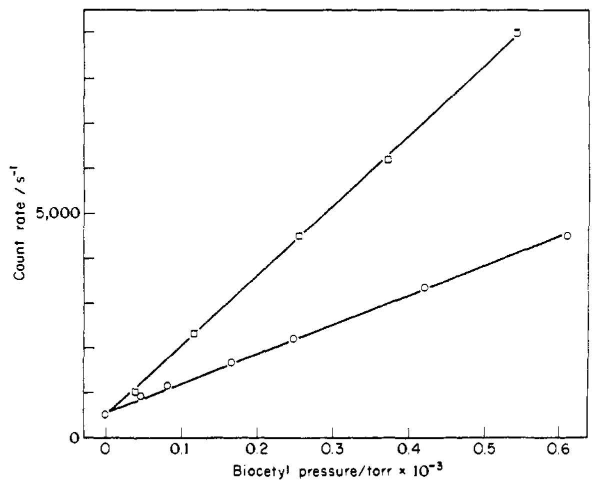


Figure 2. Calibration curves for biacetyl detection. Circles are results with 13.4 Torr of acetone excited at 330 nm as sensitizer; squares are results using 20 Torr of trifluoroacetone excited at 335 nm; temperature = 22 °C.

acetone decomposition;[24] its inclusion in the overall mechanism increases the number of phenomenologically correct explanations considerably; in particular the distinction between spontaneous decomposition of "hot triplets" and of "hot ground states" becomes largely a matter of faith.

The situation in 1,1,1-trifluoroacetone is further complicated by the possibility of three modes of photodissociation:

$$CF_3COCH_3 \rightarrow CF_3 + CH_3CO \quad (8)$$

$$CF_3COCH_3 \rightarrow CF_3CO + CH_3 \rightarrow CF_3 + CO + CH_3 \quad (9)$$

$$CF_3COCH_3 \rightarrow CF_3 + CO + CH_3 \quad (10)$$

The known instability of the trifluoroacetyl radical at room temperature[25] makes the last two processes indistinguishable. However, there is still disagreement as to which of the first two processes predominates. Sieger and Calvert[26] concluded that the second process occurred during photolysis at 313 nm, while Dawidowicz and Patrick[27] found a small amount of biacetyl as a product of photolysis of 1,1,1-trifluoroacetone at 45 °C using an unfiltered medium pressure mercury lamp and concluded that the first process occurred.

The summary presented above serves to show that in general many different explanations exist for similar phenomenologies and that in some cases conflicting results have been reported. The present work was carried out to test some of the above theories and to obtain new results relevant to a discussion of the intimate mechanism of the primary photodissociative acts in the acetone and 1,1,1-trifluoroacetone photochemical systems.

Experimental Section

(a) Materials and Gas Handling. Acetone (Baker, Analyzed Reagent, 99.7%) was purified by fractional distillation from a dry ice/acetone bath; 1,1,1-trifluoroacetone (Aldrich, 97% pure) was purified by fractional distillation from an ice water bath, the middle third being subjected to distillation from methanol slush at −92 °C. The phosphorescence decay of trifluoroacetone was the most sensitive criterion of its purity; acceptably pure samples showed no pressure quenching up to 150 Torr and no evidence for long lived phosphorescence in the tail of the decay. GLC analysis of the purified compounds (6 ft, Poropak-P, 160 °C) showed that both were at least 99.9% pure.

Carbon dioxide (Matheson, Assayed 99.995%) was used without further purification as it was found that 900 Torr did not reduce the measured quantum yield of intersystem crossing of 3 Torr of hexafluoroacetone excited at 340 nm. Fresh azomethane (Merck, Sharpe and Dohme) was used without further purification. Biacetyl (Baker) was purified by fractional distillation at 0 °C. Pure hexafluoroacetone was available from previous studies.

All compounds were stored in light tight containers on a mercury free vacuum line and were degassed at liquid nitrogen temperature before use. Pressures were measured with either of two Barratron Capacitance Manometer gauges (0-1.1 and 0-1100 Torr). All experiments were carried out at room temperature (22 ± 1 °C).

(b) Phosphorescence Decay Curves. The nitrogen laser flash apparatus described in an earlier publication[28] was used to measure phosphorescence decay curves of the ketones at various pressures and temperatures. At the lower pressures the results of 1024 flashes were averaged in a Hewlett-Packard 5480A memory display. There was no evidence for production of biacetyl during the measurements.

(c) Quantum Yields of Biacetyl Production. Biacetyl production was monitored by observing the intensity of sensitized phosphorescence excited by a pressure of the ketone at a fixed excitation wavelength (335 nm for 1,1,1-trifluoroacetone, 330 nm for acetone) and at a fixed incident intensity. The monitoring wavelengths and intensities were chosen as those at which a sufficiently high sensitivity was available with negligible production of biacetyl during the measurement period. The apparatus used is shown in Figure 1.

The phosphorimeter used a can with two equal 60° open sections and two equal closed sections; the can was rotated at 3600 rpm by a Bodine synchronous motor cooled by tap water. The phosphorimeter thus provided square wave modulation of the incident light and "box-car" detection of the emitted light, discriminating against short lived scattered light and ketone phosphorescence and fluorescence and favoring the observation of the longer lived dicarbonyl emission. A 40-mm diameter cylindrical cell made from Suprasil A was placed inside the phosphorimeter; its volume and that of associated tubing was 60 cm^3. An RCA 935 phototube viewed the transmitted radiation after the phosphorimeter. It was absolutely calibrated by azomethane actinometry in the phosphorimeter cell at 330 nm. Its wavelength dependence was obtained from results discussed under Quantum Yields of Intersystem Crossing. The product of the extinction coefficient and the effective cell length was obtained for each ketone at each wavelength of interest from the slope of Beer-Lambert plots. Such plots always gave straight lines. Photons emitted at right angles to the incident beam were amplified by an EMI 6256 photomultiplier, detected by an Ortec Model 436 discriminator, and counted for 10-s periods in an Ortec Model 720 counter. The emission detection system was calibrated by monitoring the emission from a known pressure of ketone excited at the monitoring wavelength as a function of pressure of added carbon dioxide/biacetyl mixture. The biacetyl was diluted by 3.5 × 10^3 in the carbon dioxide. In this way calibration curves, similar to those shown in Figure 2, of count rate vs. biacetyl pressure were obtained for each relevant pressure of ketone. The excitation source was a 1000 W xenon arc, driven by a Hewlett-Packard 6269B 50 A current stabilized power supply. The incident light intensity could be varied by varying the lamp current, by using neutral density filters and gauzes, by stopping the can in the open position, or by varying the

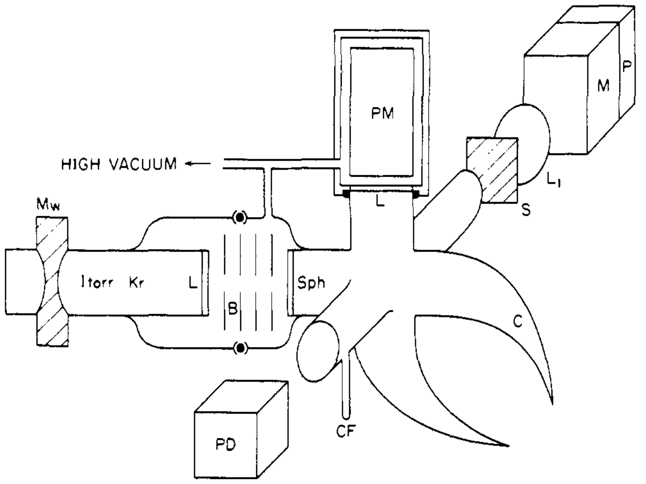


Figure 3. Apparatus to measure quantum yield of carbon monoxide production: Mw, microwave cavity; L, lithium fluoride disk; B, light baffles; PD, RCA 935 photodiode; Sph, sapphire disk; CF, cold finger; PM, EMI G-26G315 solar blind photomultiplier; C, 60 cm^3 volume quartz cell; S, shutter; L$_1$, lens; M, Bausch and Lomb 33-87-07 monochromator; P, Osram HBO 100 superpressure mercury arc.

entrance slit of the excitation monochromator. A shutter was placed before the entrance slit. The excitation monochromator was a $^1/_4$ m Schoeffel GM250 which was normally operated at 1.0-nm resolution. It was wavelength calibrated by observing the lines of a low-pressure mercury lamp in the wavelength range of interest.

In a typical experiment a pressure P of the ketone was introduced into the cell; the metal valve was closed and the background count rate was measured under the monitoring conditions; the shutter was closed and the photolysis wavelength (λ) and incident intensity were set; the shutter was open for the photolysis time during which the transmitted intensity was measured; the monitoring conditions were reset, the count rate was remeasured, and the biacetyl pressure produced by the photolysis was interpolated from ar calibration curve. The quantum yield of biacetyl production was then calculated from the formula:

$$\Phi_{\mathrm{BiA}}\,(\lambda,I_{\mathrm{A}},P,T) = \frac{M_{\mathrm{BiA}}\beta\gamma_{325}}{\beta_{325}tI_{\mathrm{T}}(10^{\epsilon lc} - 1)} \tag{1}$$

where Φ_{BiA} is the quantum yield of biacetyl production at photolysis wavelength λ (nm), ketone pressure P (Torr), rate of light absorption I_{A} (einstein cm^{-3} s^{-1}), and temperature T (°C); M_{BiA} is the amount (mol) of biacetyl produced during a photolysis of duration t (s); β is the relative quantum efficiency of the photodiode measuring the transmitted photocurrent I_{T} (A) during photolysis at wavelength λ; γ_{325} is the sensitivity of the photodiode at 325 nm in A s (einstein transmitted)$^{-1}$ and ϵl (L mol^{-1}) is the product of the effective cell length and the molar decadic coefficient of the ketone of interest at the photolysis wavelength; c is the concentration of ketone (mol L^{-1}).

In photolyses in which CO$_2$ was absent Φ_{BiA} was measured for fresh samples of ketone. In photolyses in which a large pressure of CO$_2$ was present mixtures were prepared and allowed to equilibrate for several hours; reproducible results were obtained indicating that total mixing had been achieved. Many determinations of Φ_{BiA} were then made, by measuring the increment in biacetyl pressure caused by photolysis, until the total biacetyl pressure was greater than 10^{-3} Torr. This latter technique required very precise setting of the monitoring conditions; fortunately, the lamp intensity was a precise function of the lamp current and the lamp current and photodiode stability were excellent. Thus, the greatest cause of inaccuracy in resetting the monitoring conditions, i.e., the resetting of the monitoring wavelength, could be circumvented by precisely resetting the monitoring intensity.

(d) Quantum Yields of Carbon Monoxide Productions. The production of carbon monoxide during photolysis of acetone and 1,1,1-trifluoroacetone was monitored by detecting the resonance fluorescence of the carbon monoxide produced. The apparatus used is shown in Figure 3. This apparatus was designed and built by Dr. Man Him Hui of these laboratories.

The photolysis light beam, CO resonance lamp beam, and detection photomultiplier were located on three intersecting, orthogonal axes.

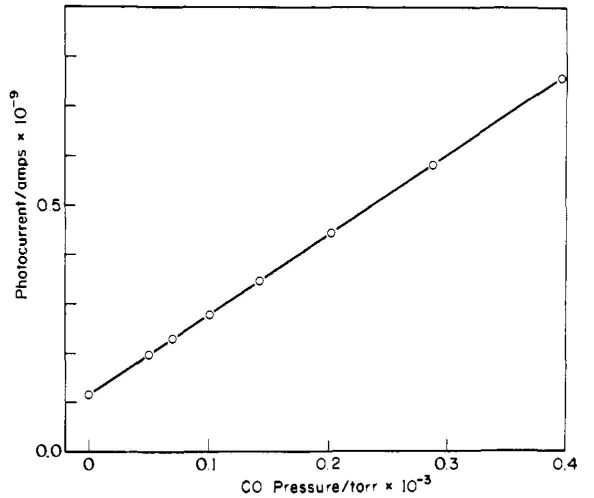


Figure 4. Calibration curve for carbon monoxide detection. Calibration was checked daily to correct for variations in resonance lamp intensity; temperature = 22 °C.

The CO resonance lamp, filled with 1 Torr of Kr and operated on impurity carbon monoxide, was driven with a microwave generator. It was found that addition of CO to the lamp gave only a transient (τ = 10 min) increase in sensitivity. Its front window was a lithium fluoride disk. CO A($^1\pi$) $\rightarrow$ X($^1\Sigma^+$), IVth positive, radiation passed through a series of light baffles and entered the photolysis cell through a sapphire window which reduced the relative amount of Kr vacuum UV radiation. Resonance fluorescence of CO in the photolysis cell was detected by an EMI g-26g315 (Rb/Te) solar blind photomultiplier biased at −2000 V and measured by a Victoreen VTE-1 picoammeter. The photomultiplier housing (EMI B215FV/RFI) was R-F shielded and it and the volume between the resonance lamp and the cell were evacuated to less than 2×10^{-6} Torr by a mercury free vacuum line. This apparatus was calibrated by measuring the scattered light in the presence of known amounts of carbon monoxide. The pressure of carbon monoxide was measured either directly by a Consolidated Engineering Corporation No. 22186 micromanometer or by expansion. During calibration runs the cell cold finger was maintained at liquid nitrogen temperature. A typical calibration curve is shown in Figure 4. The photolysis source in these experiments was either an Osram HBO 100 W super-pressure mercury arc or a Hanovia type A 550 W medium-pressure mercury lamp. A Bausch and Lomb 33-86-07 monochromator was used to select the excitation wavelength and the bandpass was 10 nm; a shutter was placed after the monochromator. The wavelength was calibrated against lines from a low-pressure mercury resonance lamp. The intensity of transmitted light was measured with a calibrated photodiode. The product ϵl was determined as before, in the photolysis cell, for each ketone at each excitation wavelength. The volume of the photolysis cell was approximately 60 cm^3; all experiments were carried out at 22 ± 1 °C.

In a typical experiment the ketone, at a pressure P in the cell, was degassed. A photolysis was then carried out for a time t and the shutter closed. The ketone was frozen down by immersing the cold finger in liquid nitrogen, the intensity of scattered light was noted and the cell was opened to the pumps; the decrease in the intensity of scattered light was converted into pressure of CO using the calibration curve. The cell was closed from the pumps and the cold finger was warmed and refrozen and the cell reopened to the pumps; any decrease in the scattered light was due to a pressure of CO occluded in the frozen ketone. In this way the total pressure of CO produced during the photolysis was obtained. It was then necessary to find the amount of CO produced by photolysis of the ketone by the resonance lamp alone during an equivalent time. This quantity was always small. The difference in these quantities (P_{CO}) was then used to obtain the relative yield of CO (Q_{CO}) from the relationship

$$Q_{\mathrm{CO}}(\lambda,I_{\mathrm{A}},P,T) = \frac{P_{\mathrm{CO}}\beta}{tI_{\mathrm{T}}(10^{\epsilon lc} - 1)} \tag{II}$$

These values were then converted to absolute quantum yields (Φ_{CO}) by comparison with Q_{CO} for 3 Torr of hexafluoroacetone at 3130 nm at room temperature (Q'_{CO}) (under these conditions Φ_{CO} has been

Table I. Quantum Yields of Biacetyl Production from Acetone and 1,1,1-Trifluoroacetone, at 22 °C

Expt No.	λ, nm	P, Torr	P_{CO_2}, Torr	I_A, einstein cm^{-3} s^{-1} × 10^{-13}	t, s × 10^2	Φ_{BiA}	D^a	A^b	B, (mol cm^{-3} s^{-1})$^{1/2}$ × 10^{-8}
(a) Acetone									
1	315	13.5	0	0.57	9	0.028	0.14	1	5.77
2	310	13.5	0	0.83	9	0.073	0.29	1	5.30
3	305	13.5	0	0.48	18	0.111	0.58	1	11.5
4	305	13.5	0	0.54	12	0.113	0.58	1	12.0
5	305	13.5	0	1.21	6	0.143	0.58	1	14.7
6	305	13.5	0	3.24	3	0.151	0.58	1	13.0
7	300	13.5	0	1.73	3	0.226	0.80	1	6.5
8	295	13.5	0	0.56	3	0.240	0.92	0.97	8.9
9	295	13.5	0	4.28	1.2	0.310	0.92	1.00^c	
10	295	13.5	885	1.60	3	0.059	0.18	0.97	11.9
11	290	13.5	0	1.56	3	0.332	0.97	1.00^c	
12	290	13.5	885	1.60	3	0.069	0.28	0.97	7.76
13	285	13.5	0	0.13	19	0.176	0.99	0.96	9.42
14	285	13.5	0	0.42	6	0.239	0.99	0.96	8.00
15	285	13.5	0	23.70	0.35	0.330	0.99	1.00^c	
16	285	13.5	885	1.53	3	0.087	0.39	0.96	12.0
17	285	13.5	885	0.54	9	0.078	0.39	0.96	14.5
18	280	2	0	0.18	18	0.222	1	0.96	7.85
19	280	13.5	0	1.36	1.8	0.295	1	0.96	5.03
20	280	13.5	0	1.86	1.8	0.323	1	0.98^c	
21	280	13.5	0	0.39	3	0.265	1	0.96	5.46
22	280	13.5	40	0.39	3	0.233	1	0.96	8.77
23	280	13.5	100	0.39	3	0.180	0.97	0.96	14.6
24	280	13.5	203	0.39	6	0.205	0.90	0.96	8.89
25	280	13.5	330	0.39	6	0.138	0.83	0.96	16.8
26	280	13.5	500	0.39	6	0.096	0.71	0.96	20.7
27	280	13.5	885	1.40	3	0.083	0.50	0.96	24.1
28	275	13.5	0	0.39	6	0.235	1	0.96	8.60
29	275	13.5	0	1.22	3	0.283	1	0.96	6.15
30	275	13.5	0	3.21	1.2	0.301	1	0.93^c	
31	275	13.5	885	1.23	3	0.088	0.58	0.9	20.4
32	270	13.5	0	0.95	3	0.276	1	0.96	2.14
33	270	13.5	885	0.98	3	0.086	0.66	0.96	29.3
34	265	13.5	0	0.24	18	0.174	1	0.86	9.98
35	265	13.5	0	0.75	6	0.239	1	0.86	6.51
36	265	13.5	0	1.80	1.83	0.286	1	0.90^c	
37	265	13.5	885	0.74	6	0.090	0.71	0.86	24.6
38	260	13.5	0	0.45	9	0.186	1	0.82	6.93
39	260	13.5	885	0.48	9	0.087	0.75	0.82	17.8
40	255	13.5	0	0.086	54	0.103	1	0.75	8.3
41	255	13.5	0	0.29	18	0.140	1	0.75	8.5
42	255	13.5	0	0.78	9	0.166	1	0.75	8.2
43	255	13.5	0	0.95	3	0.198	1	0.71^c	
44	255	13.5	600	0.95	6	0.189	0.90	0.71^c	
45	255	13.5	885	0.29	12	0.089	0.79	0.75	11.8
(b) 1,1,1-Trifluoroacetone									
46	315	20	0	0.67	36	0.0054	0.17	1.00	4.30
47	315	20	0	1.25	18	0.0070	0.17	1.00	1.05
48	315	20	0	2.67	18	0.0084	0.17	1.00	6.10
49	305	20	0	1.75	5.4	0.041	0.40	0.95	3.36
50	300	20	0	1.88	3.6	0.0713	0.54	0.94	2.72
51	295	20	0	1.80	1.8	0.119	0.67	0.94	1.60
52	295	20	900	1.88	6	0.0009	0.00	0.94	
53	290	20	0	1.66	1.8	0.144	0.77	0.92	1.25
54	285	20	0	1.40	1.8	0.162	0.85	0.90	0.96
55	285	20	0	2.97	1.8	0.187	0.85	0.90	0.58
56	285	20	0	4.58	0.9	0.200	0.85	0.90	0.26
57	285	20	0	6.15	0.6	0.204	0.85	0.90	
58	285	20	900	1.47	3.6	0.0164	0.03	0.90	
59	280	20	0	1.14	2.4	0.162	0.93	0.89	1.18
60	275	20	0	0.91	3	0.141	0.96	0.86	1.48
61	275	20	900	1.00	6	0.014	0.09	0.86	
62	270	20	0	0.68	5.4	0.120	0.99	0.81	1.58
63	265	20	0	0.43	7.2	0.106	1.00	0.78	1.44
64	265	20	900	0.50	15	0.0126	0.22	0.78	1.70
65	260	20	0	0.25	18	0.071	1.00	0.68	1.42
66	260	20	0	0.29	15	0.082	1.00	0.68	1.20

Table I *(Continued)*

Expt No.	λ,nm	P, Torr	P_{CO_2} Torr	I_A, einstein cm^{-3} s^{-1} × 10^{-13}	t, s × 10^2	Φ_{BiA}	D^a	A^b	B, (mole cm^{-3} s^{-1})$^{1/2}$ × 10^{-8}
				(b) 1,1,1-Trifluoroacetone *(Continued)*					
67	255	20	0	0.14	22.2	0.060	1.00	0.60	0.96
68	255	20	0	0.29	18	0.077	1.00	0.60	0.84
69	255	20	0	0.64	9	0.106	1.00	0.60	
70	255	20	0	0.79	5.4	0.107	1.00	0.60	
71	255	20	900	0.17	36	0.0083	0.33	0.60	

[a] Deduced from intersystem crossing quantum yield data. [b] Deduced from carbon monoxide quantum yield. [c] Deduced from eq XII.

found to be 0.5).[29] Thus:

$$\Phi_{CO}(\lambda, I_A, P, T) = \frac{0.5Q_{CO}}{Q'_{CO}} \qquad (III)$$

(e) Quantum Yields of Intersystem Crossing. The rotating can phosphorimeter was used to measure the intensity of sensitized phosphorescence (I_p) emitted by a pressure P of ketone and 0.6 Torr of biacetyl. The relative yield of intersystem crossing Q_{ISC} was calculated from:

$$Q_{ISC}(\lambda, P, T) = \frac{I_p\beta}{I_T(10^{\epsilon lc} - 1)} \qquad (IV)$$

β was calculated by noting that Q_{ISC} for the mixture 3 Torr of hexafluoroacetone + 900 Torr of carbon dioxide (Q'_{ISC}) should be independent of λ[30] and arbitrarily setting $\beta = 1$ at 280 nm. Absolute quantum yields of intersystem crossing (Φ_{ISC}) were calculated by comparison with Q'_{ISC} equal to 1.0,[30] thus:

$$\Phi_{ISC}(\lambda, P, T) = \frac{Q_{ISC}}{Q'_{ISC}} \qquad (V)$$

All measurements were made at 22 °C and with a bandpass of 1 nm.

Corrections for the direct excitation of biacetyl phosphorescence were only important at high pressures and were applied in a linear fashion, since the optical densities were low, using data obtained from mixtures of biacetyl and CO_2.

(f) Quantum Yields of Phosphorescence at Zero Pressure. Phosphorescence quantum yields (Φ_p) were measured in the rotating can phosphorimeter using the techniques described before.[1,30] Short measuring times were used to minimize biacetyl formation. Zero pressure quantum yields were obtained by extrapolating data obtained in the pressure range 0.2–2.0 Torr to zero pressure.

(g) Analysis of the Photolysis Products from 1,1,1-Trifluoroacetone Photolysis. Photolysis products were fractionated at −196, −100, −78, −16, and room temperature and were separated by GLC using a 6 ft Poropak-P column at 170 °C. Individual peaks were identified by mass-spectrometric analysis. Full experimental details will be given in a future publication.[31]

Results

The pressure dependence of the phosphorescence lifetime of 1,1,1-trifluoroacetone agreed with that found in earlier studies,[1,32] as did that of acetone.[22] Figure 5 shows the variation in the phosphorescence lifetime of acetone and acetone-d_6, excited by nitrogen laser 337-nm radiation at 22 and 50 °C as a function of ketone and carbon dioxide pressure. This pressure dependence did not affect the measured quantum yields of intersystem crossing as the biacetyl was in excess. However the quantum yields of sensitized emission at low biacetyl concentrations are sensitive to these variations. Hence, the calibration of the biacetyl production apparatus was repeated whenever the experimental conditions were varied.

As might be expected, Φ_{BiA} is a function of photolysis wavelength, pressure and rate of photon absorption, and temperature. Table I lists values of Φ_{BiA} determined for different values of the first three parameters at 22 °C. It is informative to note the short photolysis times used. The sensitivity of this technique allows one to measure Φ_{BiA} at low incident light intensities where its parametric dependence on incident intensity can be observed. Previous measurements of Φ_{BiA}, necessarily, were made at high incident flux where this dependence was absent.[3,11] Table I does not show the excellent precision of these measurements; daily repetition of the acetone/280 nm result gave identical values (±2%) of experimental readings. One can see that the total conversion in all cases was less than 0.005%. There have been no previous product quantum yield measurements at such low conversions for these systems. We also note that since the product is determined in situ, the quantum yields of biacetyl production can be measured in the presence of a large excess of inert gas, an operation which would be difficult by other routine analytical techniques. However, the method cannot be applied in the presence of triplet quenchers for obvious reasons. The decay time of the sensitized emission under all conditions was 1.45 ms.

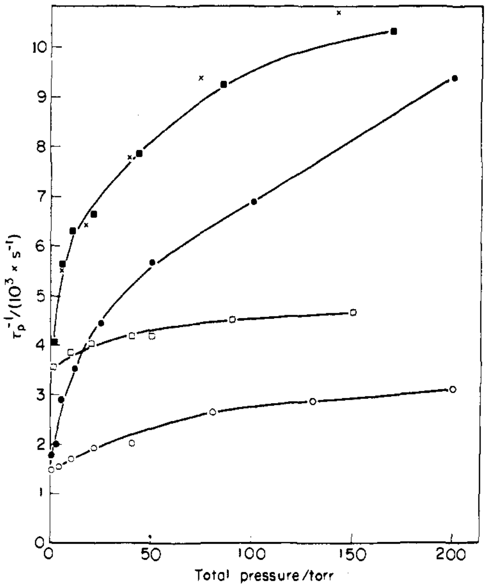


Figure 5. Values of inverse phosphorescence decay time against total pressure: circles, acetone-d_6; squares, acetone-h_6; open symbols, 22 °C; filled symbols, 50 °C. Crosses are points obtained for 5.5 Torr of acetone-h_6 in the presence of various pressures of carbon dioxide, plotted against (total pressure − ⅔ carbon dioxide pressure).

The quantum yields of carbon monoxide production (Φ_{CO}) measured in this work are shown in Table II. These quantum yields were necessarily determined at much higher rates of light absorption and at much higher percent conversions (≃0.1%). However, it was possible to measure Φ_{CO} in the presence of a known triplet quencher (0.6 Torr of biacetyl); such results are shown in Table II.

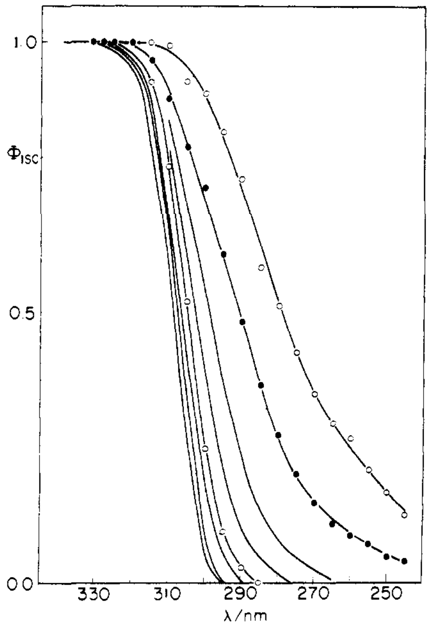


Figure 6. Values of quantum yield of intersystem crossing as a function of excitation wavelength. Curves are, from left to right: 2.0 Torr of acetone, 4.0 Torr of acetone, 4 Torr of acetone + 16 Torr of CO_2, 13.4 Torr of acetone, 4 Torr of acetone + 92 Torr of CO_2, 4 Torr of acetone + 191 Torr of CO_2, 4 Torr of acetone + 453 Torr of CO_2, and 13 Torr of acetone + 885 Torr of CO_2; curves obtained at 4 Torr of acetone + 5.2 Torr of CO_2 and 4 Torr of acetone + 40.1 Torr of CO_2 are not shown. Open circles are points obtained at 13 Torr of acetone and 13 Torr of acetone + 885 Torr of CO_2; closed circles are 4 Torr of acetone + 453 Torr of CO_2. Biacetyl pressure = 0.6 Torr; temperature = 22 °C.

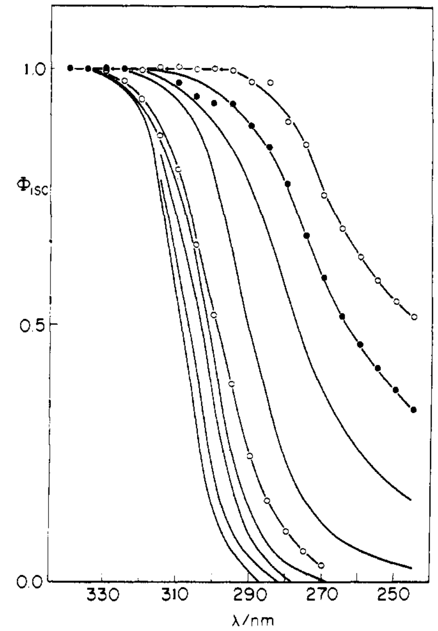


Figure 7. As Figure 6. Curves are, from left to right: 2.0 Torr of 1,1,1-trifluoroacetone (TFA), 4 Torr of TFA, 4 Torr of TFA + 11 Torr of CO_2, 20 Torr of TFA, 4 Torr of TFA + 24 Torr of CO_2, 4 Torr of TFA + 98 Torr of CO_2, 4 Torr of TFA + 272 Torr of CO_2, 4 Torr of TFA + 561 Torr of CO_2, and 20 Torr of TFA + 900 Torr of CO_2; curves obtained at 4 Torr of TFA + 3.9 Torr of CO_2 and 4 Torr of TFA + 43 Torr of CO_2 are not shown. Open circles are points at 20 Torr of TFA and 20 Torr of TFA + 900 Torr of CO_2; closed circles are points from 4 Torr of TFA + 561 Torr of CO_2. Biacetyl pressure = 0.6 Torr; temperature = 22 °C.

The effect of ketone pressure and of carbon dioxide pressure on the quantum yield of intersystem crossing at each excitation wavelength is shown in Figure 6 for acetone and in Figure 7 for 1,1,1-trifluoroacetone.

Discussion

(a) **The Mechanism.** The results presented above will be discussed within the framework of the following mechanism:

$$A + h\lambda/c \rightarrow {}^1A^* \qquad I_a \qquad (11)$$

$${}^1A^*(\rightarrow {}^3A^*) \rightarrow CX_3 + CO + CX_3 \qquad k_1 \qquad (12)$$

$${}^1A^*(\rightarrow {}^3A^*) \rightarrow CH_3CO + CX_3 \qquad k_2 \qquad (13)$$

$$\left.\begin{array}{l} {}^1A^* \rightarrow\rightarrow\rightarrow \underset{CO_2 \text{ or } A}{\quad} \rightarrow\rightarrow {}^3A \xrightarrow{a} \text{thermal decomposition} \\ \qquad\qquad\qquad\qquad\quad \xrightarrow{b} \text{ground state} \\ \qquad\qquad\qquad\qquad\quad \xrightarrow{c} \text{phosphorescence} \end{array}\right\} I_a\Phi\text{ISC} \qquad (14)$$

$$CH_3CO \rightarrow CH_3 + CO \qquad k_3 \qquad (15)$$

$$2CX_3 \rightarrow CX_3{-}CX_3 \qquad k_4 \qquad (16)$$

$$CX_3 + CH_3CO \rightarrow CX_3COCH_3 \qquad k_5 \qquad (17)$$

$$2CH_3CO \rightarrow CH_3COCOCH_3 \qquad k_6 \qquad (18)$$

where A, ${}^1A^*$, ${}^3A^*$, and ${}^3A$ are acetone or 1,1,1-trifluoroacetone molecules in the ground state, vibrationally excited first excited singlet and triplet states, and thermally distributed triplet state respectively. CX_3 is either a methyl or a trifluoromethyl radical. Reactions 12 and 13 may proceed either directly from ${}^1A^*$ or through an isoenergetic shorter lived ${}^3A^*$ (see discussion below).

We now define the rate of production of biacetyl (R) as

$$R = k_6[CH_3CO]^2 = \frac{M_{BiA}}{Vt} \text{mol cm}^{-3}\text{ s}^{-1} \qquad (VI)$$

Table II. Quantum Yields of Carbon Monoxide Production at 21 °C

Compd	P, Torr	λ, nm	I_A, einstein cm^{-3} s^{-1} × 10^{-13}	t, s × 10^2	Φ_{CO}
HFA	3	313[a]	57	6	0.50
A	13.5	240	13	6.8	0.64
A	13.5	245	29	6	0.54
A	13.5	245	29	6	0.45
A	13.5	250	34	6	0.35
A	13.5	254[a]	280	6	0.25
A	13.5	255	22	6	0.21
A[b]	13.5[b]	255	22	6	0.21
A	13.5	265	8	12	0.19
A	13.5	265	8	12	0.16
A	13.5	270	77	7	0.08
A	13.5	275	48	9	0.06
A	13.5	275	60	9	0.04
A	13.5	285	104	6	0.04
A	13.5	295	360	6	0.03
A	13.5	300	340	6	0.03
A	13.5	305	50	8	0.03
TFA	20	245	17	6	0.65
TFA	20	250	20	6	0.47
TFA	20	254[a]	160	9	0.44
TFA	20	254[a]	16	12	0.44
TFA	20	255	15	14	0.44
TFA[b]	20[b]	255	15	14	0.44
TFA	20	265	7	6	0.25
TFA	20	270	65	7	0.18
TFA	20	285	240	6	0.10
TFA	20	295	500	6	0.06
TFA	20	305	500	10	0.05
TFA	20	313[a]	200	7	0.03

[a] Photolyses with lines from medium pressure mercury arc. HFA, hexafluoroacetone; TFA, 1,1,1-trifluoroacetone; A, acetone. [b] Photolysis in the presence of 0.6 Torr of biacetyl.

and the rate of photon absorption (I_A) as

$$I_A(\lambda) = \frac{I_T(10^{\epsilon lc} - 1)\beta_{325}}{\gamma_{325}\beta V} \qquad \text{(VII)}$$

where V (cm^3) is the cell volume. There are certain assumptions about the experimental technique implicit in these two assignments. The first is that all the long lived emission observed is due to biacetyl and that the biacetyl emission is not quenched by photolysis products. This assumption is reasonable, as we have noted that the decay time of the long lived emission was constant even for considerable accumulation of biacetyl and equal to that of biacetyl (τ_p = 1.45 ms[33]).[34] The second assumption is that the radical lifetime is sufficiently long to ensure (i) that the radicals recombine within the volume of the cell (60 cm^3) and not within the volume of the light beam ($\simeq$1.5 cm^3) and (ii) that the rotation of the can corresponds to a "fast rotating sector" condition; under such condition a steady state would be reached in which the effective rates of absorption and production would be those measured. This second assumption can be shown to be a reasonable one. Thus, the radical lifetime calculated from eq VI and from estimates[12,35] of k_4 and k_3 is of the order of $\geq 10^{-1}$ s; furthermore, photolyses performed with the can stationary did not give anomalous results.

The mechanism does not include hydrogen abstraction reactions of the type:

$$CX_3 + A \rightarrow CX_3H + CH_2COCX_3$$

since, using the known values of the rate constants of these four reactions,[36] they can be shown to represent only minor pathways for loss of CX_3 at these temperatures. Such reactions are important however at higher temperatures.

Previous workers have shown that there are two different photodissociative acts in ketone photochemical systems:[3,19,20,37,38] a fast dissociation from high energy levels, and a thermal dissociation of the lowest levels of the first excited triplet. Some authors have speculated as to the pressure dependence of this latter process in acetone,[19,20] although for other ketones it is clearly first order.[38] We will return to this point when we consider the pressure dependence of Φ_{BiA}. Reaction 14a represents the steps leading to, and the thermal decomposition of, the first excited triplet state of the ketone. Most of the experiments have been performed under conditions such that this pathway is unimportant, i.e., $\Phi_{ISC} \rightarrow 0$. Moreover, this pathway represents only a minor source of products at room temperature as many workers have shown.[3,19,20] For the meantime we will neglect this reaction but will introduce corrections for it when Φ_{ISC} is high.

Given the above qualifications, inspection of the mechanism shows the following results to be generally true:

$$(1 - \Phi_{ISC}) = \Phi_{CX_3\text{-}CX_3} + \Phi_{CX_3COCH_3} + \Phi_{(CH_3CO)_2} \qquad \text{(VIII)}$$

$$\Phi_{CO} = \Phi_{CX_3\text{-}CX_3} - \Phi_{(CH_3CO)_2} \qquad \text{(IX)}$$

$$B^2C\Phi_{BiA}/I_A - B[C(2AD - 4\Phi_{BiA}) + \Phi_{BiA}]R^{1/2}/I_A + C(AD - 2\Phi_{BiA})^2 - \Phi_{BiA}{}^2 - (1 - A)D\Phi_{BiA} = 0 \qquad \text{(X)}$$

where $A = k_2/(k_1 + k_2)$, $B = k_3/k_6{}^{1/2}$, $C = k_4k_6/k_5{}^2$, and $D = (1 - \Phi_{ISC})$. Furthermore, in the limit of high intensities:

$$\Phi_{CO} = (1 - A)D \qquad \text{(XI)}$$

$$C(AD - 2\Phi_{BiA})^2 - \Phi_{BiA}{}^2 - \Phi_{BiA}D(1 - A) = 0 \qquad \text{(XII)}$$

(b) Evaluation of *A*, *B*, and *C*. Figure 8 shows that, for 13.5 Torr of acetone excited at 285 nm, the limiting value of Φ_{BiA} is attained at modest absorbed intensities; hence, all the Φ_{CO} values presented in Table II were determined within this limit. A smoothed curve of these quantum yields against wavelength was used with eq XI to calculate values of A at various excitation wavelengths. In the case of 1,1,1-trifluoroacetone, eq XI was modified to allow for the thermal triplet decomposition:

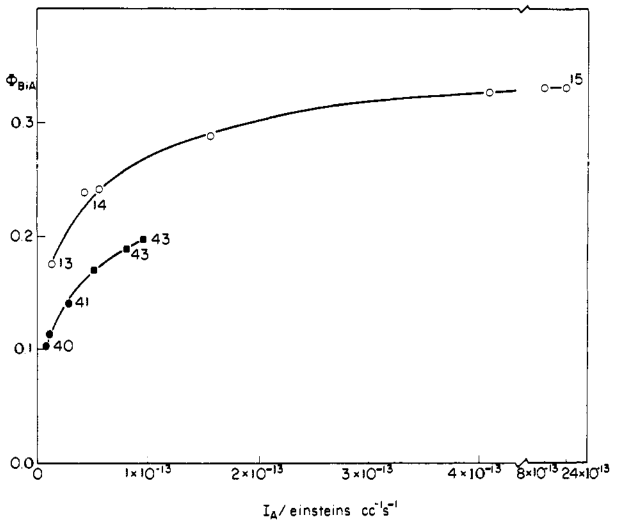


Figure 8. Quantum yield of biacetyl production in acetone as a function of absorbed intensity at 22 °C (Table I). Excitation wavelengths are 285 nm (open circles) and 255 nm (filled circles).

$$\Phi_{CO} - 0.03\Phi_{ISC} = (1 - A)D \qquad \text{(XIII)}$$

The values of A calculated from these data were used to derive an optimum value of C to fit the Φ_{BiA} data in the limit of high intensity, via eq XII. This value was 1.0 for acetone and 0.5 for 1,1,1-trifluoroacetone. The value for 1,1,1-trifluoroacetone was obtained at wavelengths where A is small and hence refers to the recombination of CF_3 and CH_3CO radicals. These constants deviate considerably from the simple collision theory value of $C = 1/4$ and this deviation is worsened by including corrections for the different mass and cross-sections of the combining radicals. The maximum value of Φ_{BiA} predicted by simple collision theory is therefore 0.25 while we observe Φ_{BiA} = 0.33 and Noyes, Ho, and Gorse[11] have observed Φ_{BiA} = 0.35 in the acetone system. Wijnen[13] has observed values of C scattered about a mean of C = 1.0 in the photolysis of methyl-d_3 acetate. These three pieces of evidence raise the interesting possibility that the recombination of two acetyl radicals may occur along a triplet potential surface. This possibility could not be excluded by Holden and Kutschke[39] as an explanation for the chemiluminescence produced on heating mixtures of gaseous ethyl hyponitrite and acetaldehyde. If this reaction were occurring in the present system it would only contribute an extremely weak background emission at the photolysis wavelength. Experiments are being performed with stronger excitation sources to test this possibility. The source of deviation from the geometric mean could however be simply experimental; a 10% error in the azomethane actinometry would yield values not far from the normal ones and further speculation is unwarranted.

The optimized values of A and C were used to derive the theoretical curves shown in Figure 9. These curves show the limiting values of Φ_{BiA} at high rates of light absorption (from eq XII) as a function of excitation wavelength. Figure 9 also shows Φ_{BiA} values determined at the highest absorbed light intensities used in this study. Good agreement is obtained for acetone data; the 1,1,1-trifluoroacetone results might be expected to be less consistent as the value of C may be wavelength dependent as more CH_3 radicals are produced at shorter excitation wavelengths. The agreement is duplicated in Table I in which the high absorbed light intensity Φ_{BiA} data are used to calculate A by substitution in eq XII. There is also good agreement with the value of A = 0.22 at 2537 Å obtained for

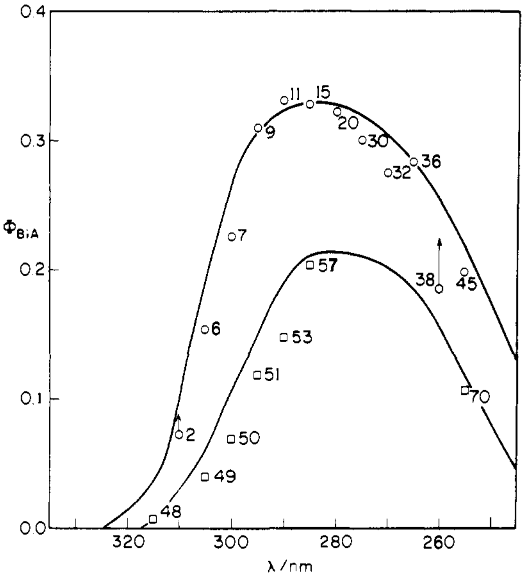


Figure 9. Theoretical quantum yield of biacetyl production at the high intensity limit (eq XII) as a function of excitation wavelength. Upper curve is for 13.4 Torr of acetone; lower curve is for 20 Torr of trifluoroacetone. The data points show the results obtained at the maximum intensity used at each wavelength (Table I): circles, acetone; squares, 1,1,1-trifluoroacetone; resolution = 1 nm; temperature = 22 °C.

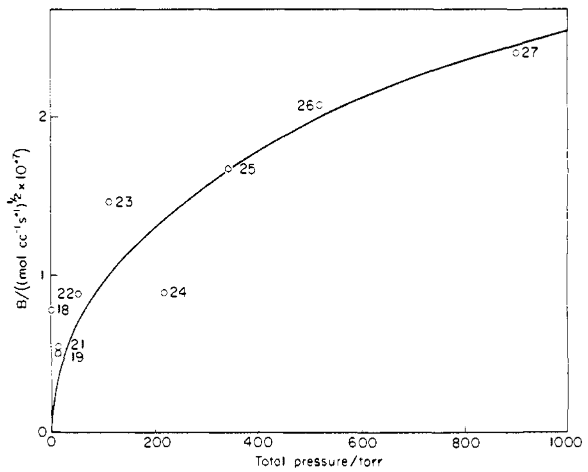


Figure 10. Pressure dependence of $k_3/(k_6)^{1/2}$. Results are from acetone excited at 280 nm, 22 °C (Table I). Solid curve is theoretical variation from ref 17.

acetone by Noyes and Dorfman.[6] The fact that A does not vary over a wide range of experimental pressures and incident light intensities, cf. experiment No. 43 and 44, Table I, is good evidence that reaction 12 proceeds directly or through the production of an extremely short lived acetyl radical. The postulate of "hot" acetyl radical production invoked by other authors[16] to explain certain aspects of the acetone photochemical system would not appear to be valid. However, the possibility that reaction 12 proceeds through the production of a predissociating electronically excited state of the acetyl radical cannot be discarded. Thus, model calculations on the formaldehyde photolysis system show that the ground and first excited singlet states correlate, along the H + HCO dissociation path, with the ground and first excited H + HCO limits, respectively.[40] The first triplet state correlates with ground state H + HCO but exhibits a barrier of 24 kcal mol^{-1}. In acetone these correlations are likely to be equivalent, but unfortunately no spectroscopic data exist for the acetyl radical. The only data available seem to be the CNDO/2 calculations of White, Yarwood, and Santry[41] who calculate the first excited state to be $^2A''$ at an energy of 0.13 eV above the $^2A'$ ground state. Clearly, decomposition from such a low lying excited state is thermodynamically impossible but would be probable at the energies at which A has nonnegligible values.

Further evidence against the production of "hot" acetyl radicals is provided by the constancy of the values of B deduced from eq X. Inspection of the equation in the limit of high absorbed intensities shows the negative root to be proper $((-b - [b^2 - 4ac]^{1/2})/2a)$. Values of B computed from this relationship using Φ_{BiA} data obtained at low light intensities are shown in Table I. We note that there is no obvious increase in these values as the energy of the exciting radiation is increased by 19 kcal mol^{-1} (300-250 nm); this is good evidence that all observable acetyl radicals are thermalized at 13 Torr. The scatter in these values is inherent in the number of experimental measurements needed to derive the rate constant ratio. Values obtained when most experimental conditions are kept constant are subject to less error. Figure 10 shows the pressure dependence of B determined from a run in which only the carbon dioxide pressure was varied; the solid curve shows the theoretical curve derived by Watkins and Word[17] for the pressure dependence of k_3. There is reasonable agreement at high pressures but serious disagreement at pressures below 10 Torr. This observation does not support the contention that a heterogeneous production of biacetyl is important at low pressures;[9,10] however, it does seem likely that the scaling of the theoretical pressure dependence is incorrect. Thus, the theoretical curve of Figure 10 approaches a value of B of 38 × 10^{-8} (mol cm^{-3} s^{-1})$^{1/2}$ at infinite pressure while the data points extrapolate (B^{-1} vs. inverse total pressure) to a B value of 26 × 10^{-8} (mol cm^{-3} s^{-1})$^{1/2}$ at infinite pressure. Table III compares these values with values from the literature. The disparity in the results obtained from acetone and 1,1,1-trifluoroacetone photolysis almost certainly reflects the breakdown of the initial assumption that CH_3 and CF_3 recombination reactions have the same rate constants. In conclusion we note that previous studies of the pressure effect on biacetyl and carbon monoxide production[9,10] and subsequent reinterpretations of these results[8,15,16] have neglected pressure-induced vibrational relaxation to the thermal triplet and the possibility that the thermal decomposition of this triplet state may be pressure dependent.[21] Our results though were obtained at 280 nm where the intersystem crossing yield is small and such effects are minimized; furthermore the results were obtained at low ketone pressures where the radical/molecule concentration ratio is high. Vibrational relaxation reduces the decomposition yield and reduces this ratio favoring radical molecule reactions. Products of the type:

Table III. Values of $k_3/(k_6)^{1/2}$

Source	P, Torr	T, K	B, (mol cm^{-3} s^{-1})$^{1/2}$ Obsd	Calcd[d]
Ref 8	∞	295	~	3.5×10^{-8}
Ref 15	∞	295	~	3.6×10^{-10}
Ref 16	∞	295	~	1.3×10^{-6}
Ref 17	∞	295	~	6.3×10^{-7}
Ref 13	30-60	303	3.9×10^{-7}	~
Ref 6	100	298	4.8×10^{-8}	~
This work[a]	13	295	8.0×10^{-8}	~
This work[b]	∞	295	2.8×10^{-7}	~
This work[c]	20	295	1.3×10^{-7}	~

[a] Value obtained from average of all acetone data at 13 Torr. [b] Value obtained by extrapolation to infinite pressure. [c] Value obtained from average of all 1,1,1-trifluoroacetone data at 20 Torr. [d] Value calculated from Arrenhius equation, assuming $k_6 = 2 \times 10^{13}$ cm^3 mol^{-1} s^{-1}.

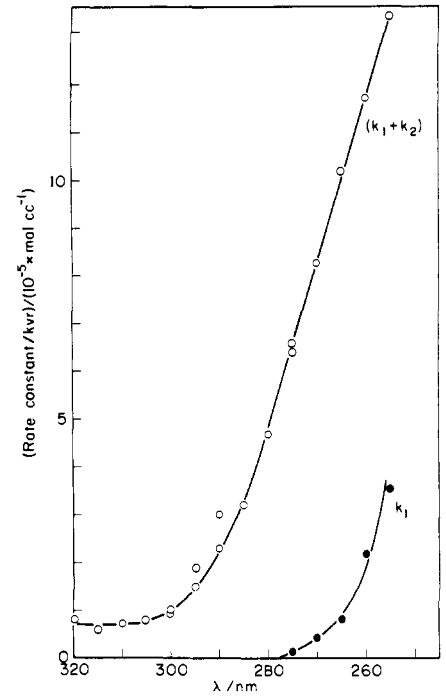


Figure 11. Values of excited singlet state nonradiative rate constant/stabilization ratios as a function of excitation wavelength; 13.5 Torr of acetone at 22 °C.

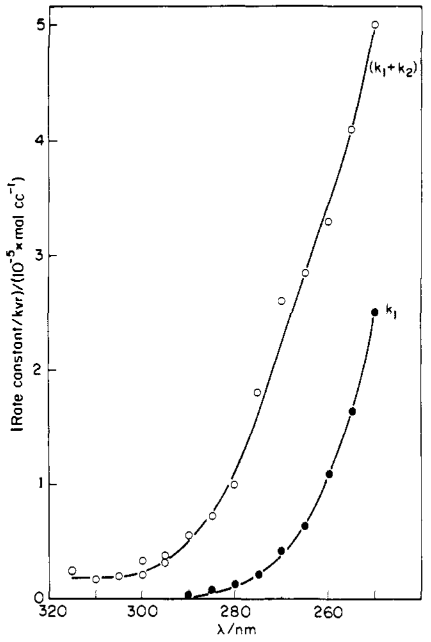
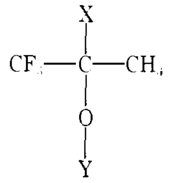


Figure 12. Values of excited singlet state nonradiative rate constant/stabilization ratios as a function of excitation wavelength; 20 Torr of 1,1,1-trifluoroacetone at 22 °C.



$$\mathrm{CF_3{-}\overset{\displaystyle X}{\underset{\displaystyle \underset{\displaystyle Y}{O}}{C}}{-}CH_3}$$

where X and Y may be CF_3, CH_3, or CH_3CO, have been isolated after 1,1,1-trifluoroacetone photolyses at high ketone pressures but are absent at low pressure.[31]

(c) **Evaluation of ($k_1 + k_2$).** An estimate of the magnitude of ($k_1 + k_2$) can be obtained from the data in Figures 6 and 7. If we assume a single step deactivation in reaction 14, a valid assumption at high CO_2 pressures and when ($k_1 + k_2$) is a sharply increasing function of internal energy, then:

$$\Phi_{ISC} = \Phi^0_{ISC} + k_{vr}[M](1 - \Phi^0_{ISC})/(k_1 + k_2 + k_{vr}[M]) \qquad (XIV)$$

where Φ^0_{ISC} is the intersystem crossing yield at zero pressure, k_{vr} is the effective deactivation rate constant in reaction 14, and [M] is the total pressure. Φ^0_{ISC} was estimated by extrapolating the data of Figures 6 and 7 to zero pressure and the ratio $(k_1 + k_2)/k_{vr}$ was then found from the slopes of plots of $(1 - \Phi^0_{ISC})/(\Phi_{ISC} - \Phi^0_{ISC})$ against $[M]^{-1}$. These ratios, together with the ratios k_1/k_{vr} found by substitution with the relevant values of A, are shown in Figure 11 for acetone and in Figure 12 for 1,1,1-trifluoroacetone.

The pressure-induced enhancement of the intersystem crossing quantum yield gives information about the lifetime of the longest lived excited state involved in the relaxation pathway of the optically formed excited state to the thermalized levels of the triplet. An estimate of this lifetime can be made by assuming reasonable values of k_{vr}. In the case of 1,1,1-trifluoroacetone substitution of $k_{vr} = 2 \times 10^{13}$ cm^3 mol^{-1} s^{-1} leads to $(k_1 + k_2)^{-1}$ values (Figure 12) which agree quantitatively with the recently measured fluorescence lifetime of isolated molecules[42] of this compound. The implication of this fortuitous agreement and the fact that the decomposition product biacetyl is quenched by carbon dioxide in the manner predicted by the mechanism is either (a) that decomposition reactions 12 and 13 occur directly from the excited singlet state or (b) that decomposition occurs from excited states reached from the excited singlet state, excited states whose lifetimes are much shorter than the excited singlet state. Distinction between (a) and (b) is largely semantic in that both describe the available data equally well, but its implications are important. Thus, if (a) were true, the measurement of singlet state emission decay times would provide tests for unimolecular spontaneous decomposition rate constants; such tests are not possible if (b) is true. In an earlier paper[30] it was concluded that (b) was true in the hexafluoroacetone photochemical system. This conclusion was based upon the form of the zero-pressure quantum yield as a function of wavelength, and on the pressure induced enhancement of phosphorescence. 1,1,1-Trifluoroacetone shows entirely analogous results; indeed the results for this molecule are even less ambiguous than those for hexafluoroacetone for the following reasons. 1,1,1-Trifluoroacetone thermal triplet and singlet ($\tau_p = 260$ μs[32] and $\tau_F = 4$ ns[37]) are both shorter lived than their hexafluoroacetone counterparts ($\tau_p = 3.4$ ms and $\tau_F = 84$ ns); thus there exists a wider pressure regime in which we can study 1,1,1-trifluoroacetone vapor such that the singlet state is collision free and the triplet state is "wall free". However, even given this greater range of pressures, no evidence was found in the pressure enhancement of 1,1,1-trifluoroacetone phosphorescence (Figure 13) for the involvement of excited states with lifetimes other than those of the excited singlet, at any excitation wavelength. The zero-pressure phosphorescence quantum yield of 1,1,1-trifluoroacetone as a function of excitation energy is shown in Figure 14, together with the zero-pressure intersystem crossing quantum yields deduced by extrapolating the data of Figure 7. The form of the fall-off in these curves as the excitation energy is raised can be explained by either (or both) of two mechanisms analogous to (a) and (b): (c) decomposition or internal conversion compete more efficiently with intersystem crossing as the internal energy is raised and (d) triplet states formed with energies greater than a certain minimum energy decompose with unit efficiency at all pressures, the fall-off region being explained by the transfer of ground state thermal energy to the excited state. It was concluded that (d) was more

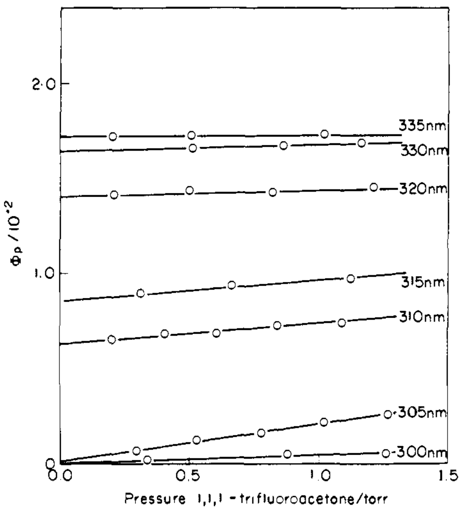


Figure 13. Pressure dependence of the phosphorescence quantum yield of 1,1,1-trifluoroacetone (Φ_p) at various excitation wavelengths. Resolution = 1 nm, temperature = 22 °C.

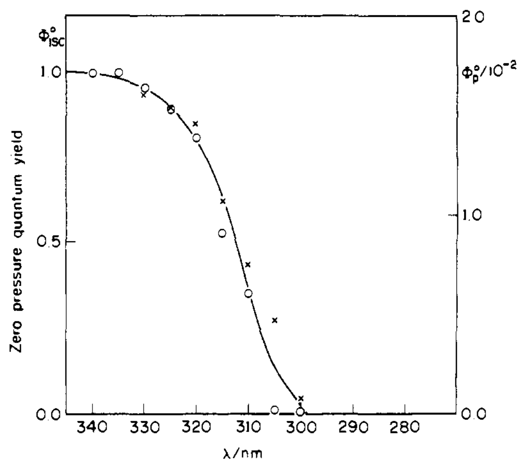


Figure 14. Values of zero-pressure phosphorescence yield (circles) and zero-pressure intersystem crossing yield (crosses) as a function of excitation wavelength: 1,1,1-trifluoroacetone, 22 °C, 1 nm resolution. A pressure of 0.6 Torr of biacetyl was used to measure the intersystem crossing yield.

likely in hexafluoroacetone[30] because assumption (c) required an unreasonable form for the wavelength dependence of the intersystem crossing rate constant, and the minimum energy deduced by assuming (d) agreed precisely with the known activation energy for the loss of phosphorescence.[43] The first condition is true for trifluoroacetone, while data pertinent to the second point are sparse. Ausloos and Murad[44] report an activation energy of 11-12 kcal mol^{-1}; however, their sample is known to have contained a triplet quencher.[1] Hackett and Phillips[45] report the zero-zero energy of 1,1,1-trifluoroacetone triplet to be 75 kcal mol^{-1}, although this value would seem to be low by comparison with those of acetone[46] (80 kcal mol^{-1}) and hexafluoroacetone (75 kcal mol^{-1}).[30] These values lead to an estimate of the decomposition barrier in triplet 1,1,1-trifluoroacetone at 87 kcal mol^{-1}; the value estimated from Figure 14 is 94 kcal mol^{-1}. Clearly more precise data are needed.

There are three sources of values of $(k_1 + k_2)$ for acetone in the literature: the fluorescence decay times measured by Breuer and Lee[47] for acetone excited at 313, 295, and 280 nm (k_{NR} = 3.7, 4.8, and 5.9 × 10^8 s^{-1}), the wavelength dependence of the fluorescence quantum yield of acetone,[48] and the spontaneous decomposition lifetimes of O'Neal and Larson.[21] The latter set of values was determined from the pressure dependence of the acetone phosphorescence quantum yield excited at various wavelengths; such values are equivalent to the values reported in Figure 11, which were obtained from the pressure dependence of the intersystem-crossing quantum yield. Fortunately both sets of values agree. However, O'Neal and Larson[21] assign the fast dissociative pathway to the spontaneous decomposition of the triplet state and therefore fit the values of $(k_1 + k_2)$ to an RRK formula of the type:

$$(k_1 + k_2) = 10^{11}\left(\frac{E - Ec}{E}\right)^{s-1}$$

This procedure would only be justified if the singlet-triplet intersystem crossing was the only process depleting the vibrationally excited singlet state and if its rate constant was much greater than the spontaneous decomposition rate. Unfortunately, the directly measured singlet lifetimes are greater than or equal to the values of $(k_1 + k_2)^{-1}$. It would seem reasonable to assign these rate constants as in hexafluoroacetone and 1,1,1-trifluoroacetone to excited singlet state nonradiative processes and to argue that the agreement with the RRK calculations was purely fortuitous.

The values of the total singlet state nonradiative rate estimated from the fluorescence quantum yield data reported by Lee[48] do not increase with internal energy to the same extent as $(k_1 + k_2)$. A possible explanation for this behavior may be given. The fluorescence quantum yields were measured in the presence of 4 Torr of oxygen and 50 Torr of cyclohexane. One can see from Figure 6 that 50 Torr of carbon dioxide is sufficient to relax some acetone states to the low-lying thermal levels of the triplet. Cyclohexane should be a more efficient vibrational relaxer of acetone than carbon dioxide, and if the trend in $(k_1 + k_2)$ does represent singlet state nonradiative rate constants, it is necessary to remove far less vibrational energy to enhance the fluorescence quantum yield excited at short wavelengths than to enhance the corresponding intersystem crossing quantum yield. Clearly, further work is needed to check this point.

(d) Energetic Considerations. The minimum energy barrier for decomposition of acetone triplet can be estimated in a manner analogous to that for 1,1,1-trifluoroacetone and hexafluoroacetone by extrapolating the data of Figure 6 to zero pressure. A value of 95 kcal mol^{-1} is obtained (hexafluoroacetone 90 kcal mol^{-1}, 1,1,1-trifluoroacetone 94 kcal mol^{-1}). The experimentally observed activation energy appears to be 11 kcal mol^{-1},[21,49] although Cundall reports 6 kcal mol^{-1} and Larson and O'Neal report 17 kcal mol^{-1}.[20] These values combined with the triplet energy lead to barrier heights of 86-97 kcal mol^{-1}.

Figures 11 and 12 can be used to define minimum energies for the occurrence of reaction 12. For acetone this energy is 104 kcal mol^{-1} and for 1,1,1-trifluoroacetone the energy is 98 kcal mol^{-1}. These energies are maximum values as the pressures used were not quite in the collision-free regime. The 1,1,1-trifluoroacetone data are possibly obscured by the sequential production and decomposition of a trifluoroacetyl radical. If one regards this sequential route as the only mechanism of reaction 12 then the curves of k_1 and k_2 vs. excitation energy can be used to derive the probability of the CH_3-$COCF_3$ relative to the probability of the CF_3-$COCH_3$ bond breaking. This probability is 0.00 at energies near the critical energy and would be 0.11, 0.15, 0.21, and 0.33, at energies of 2, 6, 9, and 12 kcal mol^{-1} above the critical energy. However, reaction 12 undoubtedly occurs at least in part by the direct route and these probabilities are even smaller.

(e) Decomposition from the Thermalized Triplet. All the results considered above have been obtained in regions in which decomposition of the thermal triplet is unimportant. Larson and O'Neal[21] consider the decomposition of the thermal triplet of acetone to be a unimolecular reaction in its pressure fall-off region; this interpretation has been questioned recently[50] as the A factor obtained disagrees by a factor of 10^6 with the A factor for similar bond cleavages. The present study has revealed two pertinent pieces of information. Larson and O'Neal's contention is supported by the fact that carbon dioxide has the same effect on the phosphorescence lifetime as does acetone and by the fact that the Arrhenius parameters for the pressure induced reaction in acetone-d_6 are exactly equivalent for those in acetone-h_6; only a small secondary isotope effect would be expected if this reaction were dissociation. However, it was our observation that addition of carbon dioxide to 13 Torr of acetone always decreased the rate of production of biacetyl. Larson and O'Neal's[21] mechanism would demand a large increase in this rate at 315 nm where $\Phi_{ISC} \rightarrow 1.0$ and the acetyl production rate is low. It is obvious that much more work is needed to fully explain these observations.

Conclusions

We have presented evidence for two modes of photodissociation of acetone and 1,1,1-trifluoroacetone. Energy thresholds for these dissociations are

$$CH_3COCH_3 \left\{ \begin{array}{ll} \rightarrow CH_3 + CH_3CO & E_{min} = 95\ \text{kcal mol}^{-1} \\ \rightarrow CH_3 + CO + CH_3 & E_{min} = 104\ \text{kcal mol}^{-1} \end{array} \right.$$

$$CF_3COCH_3 \left\{ \begin{array}{ll} \rightarrow CF_3 + CH_3CO & E_{min} = 94\ \text{kcal mol}^{-1} \\ \rightarrow CF_3 + CO + CH_3 & E_{min} = 98\ \text{kcal mol}^{-1} \end{array} \right.$$

We have failed to observe evidence for excited states with lifetimes intermediate between the excited singlet and thermal triplet.[51] This point was based upon the pressure dependence and equivalence of the phosphorescence and intersystem crossing yields at low pressures; we plan to carry out a more direct search for such states by measuring emission decay profiles at low pressures. The failure to observe long-lived triplet states at short excitation wavelengths may be explained in two ways, by an increase in excited singlet state nonradiative processes other than intersystem crossing,[23] or by a decrease in vibrationally excited triplet lifetime.[30] We have advanced evidence which supports the second possibility.

Acknowledgments. It appears to be characteristic of the photochemistry of the simple carbonyl and dicarbonyl molecules that constant reinvestigation leads to constant reinterpretation; in this we acknowledge our debt to the earlier work of W. A. Noyes and his co-workers, whose conclusions have provided the base for this study. We are very grateful to Dr. Man Him Hui for allowing us to use his apparatus and to Dr. R. A. Back who pointed out the classical error in the first draft of this paper and who with Dr. K. O. Kutschke contributed to many helpful discussions.

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