

TEMPERATURE DEPENDENCE OF THE TRIPLET LIFETIME OF BIACETYL IN THE GAS PHASE

COLMAN O CONCHEANAINN and HOWARD W. SIDEBOTTOM

Department of Chemistry, University College Dublin, Dublin (Eire)

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Summary

The lifetime of electronically excited triplet 3A_u biacetyl was determined in the gas phase as a function of temperature (25 - 189 °C) and of concentration (2.5×10^{-6} - 1.35×10^{-3} mol l⁻¹). The triplet lifetime was observed to decrease with increasing temperature and, over the range of concentrations investigated, was shown to be independent of concentration for temperatures less than 123 °C. However, at higher temperature the lifetimes were found to decrease with increasing concentration. This dependence did not follow simple Stern-Volmer behaviour, since the lifetime reached a value which was insensitive to further increases in concentration. The results were rationalized in terms of the decomposition of thermalized triplets, which is a unimolecular pressure-dependent process with a high pressure limiting rate constant k_∞ of $10^{11.3 \pm 0.5} \exp \{-(13.9 \pm 0.8 \text{ kcal mol}^{-1})/RT\} \text{ s}^{-1}$.

The lifetime data at elevated temperatures provide evidence that the quantum yield of triplet formation from the initially formed singlet state is constant and close to unity in the range 25 - 119 °C. The data also indicate that some product formed during the photolysis of biacetyl at wavelengths greater than 400 nm is an efficient quencher of the triplet state and that this effect increases with reaction temperature.

1. Introduction

Biacetyl has been used widely as a gas phase emission standard and as a triplet energy acceptor in the study of triplet molecule participation in the photochemistry of other molecules. Extensive studies [1, 2] have been made on both the liquid and vapour phase photochemistry of biacetyl, and the basic mechanisms of the photochemical and photophysical processes are well established at room temperature. However, comparatively little information is available concerning the temperature dependence of these processes.

Several investigations on the effect of temperature on the photolysis of biacetyl have been reported. Noyes and coworkers [3, 4] have found that the quantum yield of fluorescence changes little with temperature whilst the

phosphorescence yield decreases markedly over the range 26 - 182 °C. Similar results have been observed by Groh [5] who showed that phosphorescence is completely absent at 200 °C, leaving only the fluorescence emission. A small reduction in the triplet lifetime at 79 °C is consistent with the aforementioned phosphorescence yield data [6]. Excitation by low intensity light at 435.8 nm causes negligible dissociation of biacetyl at room temperature. However, at temperatures greater than 100 °C a first order dissociation process becomes important [7, 8]. The lack of a temperature effect on the fluorescence yield, together with the decrease in phosphorescence at elevated temperatures, suggests that this dissociation occurs from the triplet state. Finally, a rapid quenching of both the phosphorescence and the primary dissociation of biacetyl vapour has been observed [8, 9] following excitation at 435.8 nm and at temperatures in the range 100 - 150 °C. Attempts to identify the reaction product responsible for these effects were unsuccessful. It has been suggested [9, 10] that an enolic form of biacetyl, which quenches the triplet state by some chemical means, is responsible for the observed effect.

This work is concerned with the lifetime of the triplet state of biacetyl in the gas phase over relatively wide ranges of concentration and temperature. It was hoped that the results would provide estimates of the pre-exponential factors and activation energies associated with some of the radiationless processes.

2. Experimental

A conventional mercury-free greaseless vacuum system was used for all the experiments. Pressure measurements were made using a Pyrex spiral gauge as a null instrument. A thermal gradient pump in series with the cell was used to mix the reactants.

Biacetyl (Fluka, Puriss) had a stated purity of 99.5% and was distilled in the vacuum system. The fraction which was volatile at -63 °C (CHCl_3 melt) was rejected, a portion which distilled at -23 °C (CCl_4 melt) was retained and the residue was rejected. The retained portion was degassed thoroughly by bulb-to-bulb distillation and stored under liquid nitrogen. Carbon dioxide (Matheson Gas Products, Research Grade) with 99.995% stated purity was distilled in the vacuum line prior to use.

Triplet 3A_u biacetyl molecules were produced via intersystem crossing from the first excited singlet state 1A_u , when biacetyl was irradiated close to the 0-0 band of the $^1A_u \leftarrow ^1A_g$ absorption under non-collision-free conditions. A 0.5 μs pulse of light from a flash-lamp-pumped tunable dye laser (Electrophotonics Ltd., Model 23) was used to excite biacetyl to its first excited singlet state. The laser was tuned using Coumarin 2 as the laser dye to enable excitation at 440 nm with a bandwidth of less than 1 nm. The laser output power was measured with a thermopile detector (Laser Instruments Ltd., Model 14 NO). The output energy available per pulse was about 2 mJ. In this work the beam was attenuated by a factor of up to 1000

through the use of neutral density filters, to avoid high concentrations of biacetyl triplet and to ensure the unimportance of triplet-triplet annihilation reactions [11].

The T-shaped Pyrex luminescence cell (10 cm in length and 516 ml in volume) had front and side windows of diameter 5 cm and was housed in an insulated air furnace. The temperature was controlled to better than ± 0.2 °C and was measured using thermocouples attached to the cell. Phosphorescence from excited biacetyl molecules was detected perpendicular to the incident laser beam using an E.M.I. 9659 QB photomultiplier fitted with a 500 nm long-pass filter (Corning CS 3-69). The intensity-time record of the phosphorescence decay was recorded on an oscilloscope, photographed and analysed.

All continuous photolysis experiments were carried out using a 150 W xenon short arc lamp (Ushio UXL-151D) powered from its own intensity-stabilized power supply. Quartz lenses were used to produce an approximately parallel beam of light of diameter 5 cm and the incident light was restricted to wavelengths greater than 400 nm by a long-pass filter (Corning CS 3-73). The lamp and its associated lens system was attached to an optical bench so that it could be moved with precision to allow lifetime measurements to be made at various intervals using the laser system.

3. Results

The lifetime of the first excited triplet state of biacetyl was determined in the range 25 - 189 °C in pure biacetyl and in mixtures with carbon dioxide. Representative data for the lower temperature studies are given in Table 1 and the lifetimes determined at higher temperatures are shown in Fig. 1. At the low laser intensities employed decays of phosphorescence were clearly exponential in character over at least three lifetimes. Also a further reduction in excitation intensity by a factor of four did not affect the measured lifetimes, indicating that this intensity is well below the level at which significant depopulation of the triplet results from triplet-triplet annihilation [11].

A considerable decrease in the lifetime with increasing temperature was observed. For temperatures up to 123 °C the phosphorescence decays were found to be insensitive to the concentration of biacetyl or of added carbon dioxide over the range 2.5×10^{-5} - 1.35×10^{-3} mol l⁻¹. There was, however, a marked reduction from the high concentration near-constant value of the biacetyl triplet lifetime for experiments at lower concentrations. Addition of carbon dioxide caused a return of the observed lifetime to the value found for biacetyl alone at the concentration of the combined gases. These observations can be rationalized in terms of biacetyl triplet deactivation at the cell wall [12, 13].

At higher temperatures the triplet lifetimes decreased with increasing concentration. The decrease in lifetime with concentration was non-linear and the decay rate appeared to approach a maximum limiting value (Fig. 1).

TABLE 1

Inverse triplet lifetime of biacetyl vapour as a function of biacetyl and carbon dioxide concentration from 25 to 123 °C

Temperature (°C)	Reactant concentration ($\times 10^{-4}$ mol l $^{-1}$)		Inverse triplet lifetime ($\times 10^2$ s $^{-1}$)
	[(CH ₃ CO) ₂]	[CO ₂]	
25	0.0050	0.0	16.7
	0.0050	10.8	5.71
	0.0163	0.0	9.70
	0.0163	10.8	5.68
	0.285	0.0	5.71
	0.987	0.0	5.58
	6.40	0.0	5.59
	13.5	0.0	5.87
	13.5	10.8	5.88
44	3.02	0.0	6.57
56	0.608	0.0	6.91
	13.5	0.0	6.91
62	1.61	65.6	7.66
	2.11	0.0	7.68
73	12.6	0.0	9.38
74	1.61	65.6	9.22
	3.02	0.0	9.32
84	1.61	65.6	11.4
	3.02	0.0	11.4
	9.38	0.0	11.4
93	6.95	0.0	16.1
99	3.02	0.0	16.0
101	12.6	0.0	18.0
105	0.608	0.0	16.9
112	1.61	65.6	27.2
	3.02	0.0	26.2
	5.80	0.0	27.4
123	1.61	65.6	38.6
	2.96	0.0	35.2
	13.4	0.0	37.4

This effect was confirmed on addition of the inert diluent carbon dioxide to various concentrations of biacetyl. Again the inverse triplet lifetime increased steadily before reaching a maximum (Fig. 2). As a check on the effect of a high number of laser pulses on a particular sample, and also on any possible effects caused by products arising from thermal decomposition of biacetyl, a series of experiments was carried out at 189 °C in which the sample was repeatedly pulsed (approximately 1000 pulses) and was allowed to remain in

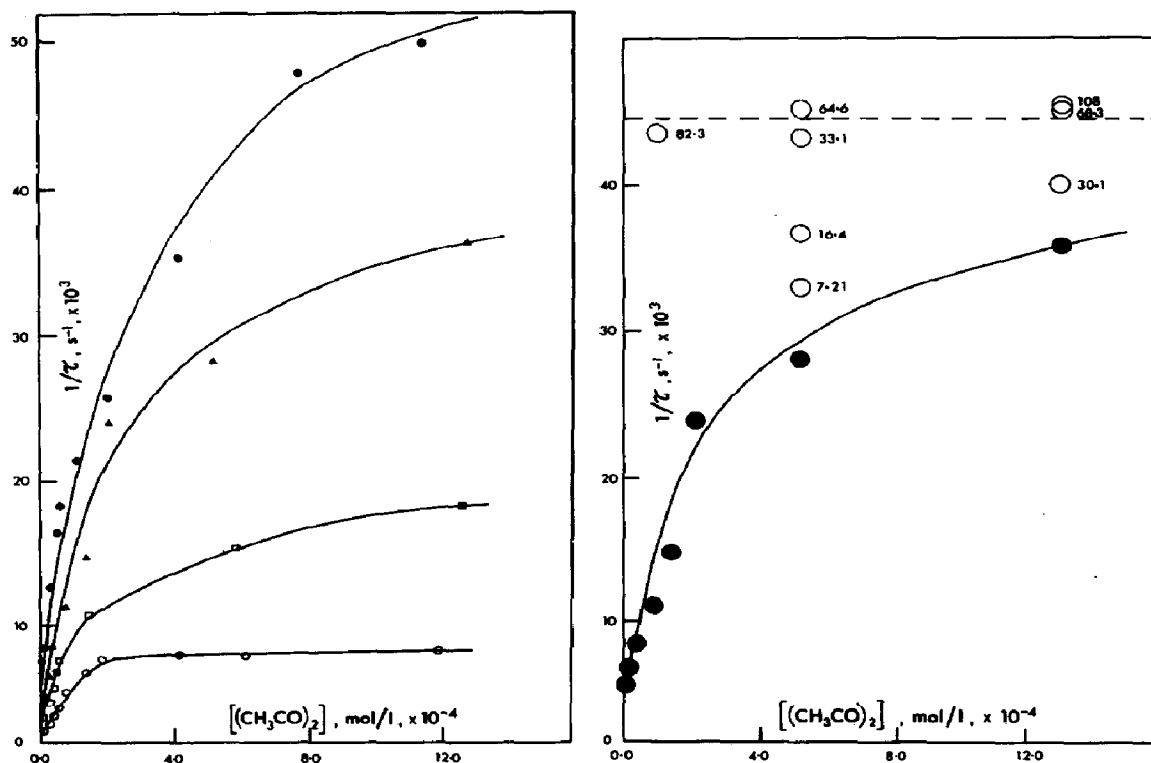


Fig. 1. The inverse triplet lifetime vs. the biacetyl concentration for excitation at 440 nm: \circ , 144 °C; \square , 161 °C; \triangle , 177 °C; \bullet , 189 °C.

Fig. 2. The effect of the addition of carbon dioxide on the inverse triplet lifetime at 177 °C: \bullet , pure biacetyl; \circ , addition of various quantities of CO_2 ($\times 10^{-4}$ mol l $^{-1}$).

the reaction cell for about 12 h. The results indicated that the lifetime remained constant during this series of experiments. Similarly in a number of experiments the lifetime of a particular sample was determined in the heating cycle and then remeasured as the system cooled. In each case the remeasured lifetime was in good agreement with data obtained in the initial sequence, so that problems associated with the formation of a quenching product were not encountered.

A series of experiments was carried out in order to determine the quantum yield of triplet production as a function of temperature. The relative initial intensity I_p^0 of phosphorescence, as measured by the photomultiplier response immediately after the laser pulse, is directly proportional to the concentration of triplets formed by intersystem crossing from the singlet state. Relative initial intensities were determined by extrapolating the semi-logarithmic phosphorescence decay plots to zero time. Since the extinction coefficient for biacetyl is virtually independent of temperature under the experimental conditions used in this work, the absorbed light intensity is directly related to the incident laser intensity I_0 for experiments carried out with a fixed concentration of biacetyl. Because the values of I_0 varied from

experiment to experiment by as much as 15%, it was necessary to determine I_0 for each run. The ratio I_p^0/I_0 given in the last column of Table 2 is therefore proportional to the quantum yield of triplets formed from singlets following the laser pulse.

The phosphorescence lifetime was also determined at various intervals during continuous photolysis experiments. Photolyses were carried out at wavelengths greater than 400 nm and in the temperature range 25 - 177 °C. The results shown in Fig. 3 indicate that the triplet lifetime decreased with increasing photolysis time and that the effect was more pronounced at high temperatures.

4. Discussion

The primary processes following excitation of biacetyl close to the origin of the first excited singlet state can be conveniently discussed in terms of the following mechanism:

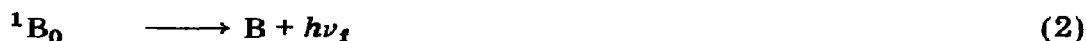


TABLE 2

Relative quantum yield of triplet production as a function of temperature^a

Temperature (°C)	Incident laser intensity I_0 in arbitrary units	Initial phosphorescence intensity I_p^0 in arbitrary units	I_p^0/I_0
25	44.2	74.3	1.68
56	40.7	66.0	1.62
69	41.5	70.3	1.69
84	38.8	68.3	1.76
93	42.5	68.8	1.62
101	39.8	67.3	1.69
119	41.1	65.0	1.58

^a $[(CH_3CO)_2] = 6.95 \times 10^{-4} \text{ mol l}^{-1}$.

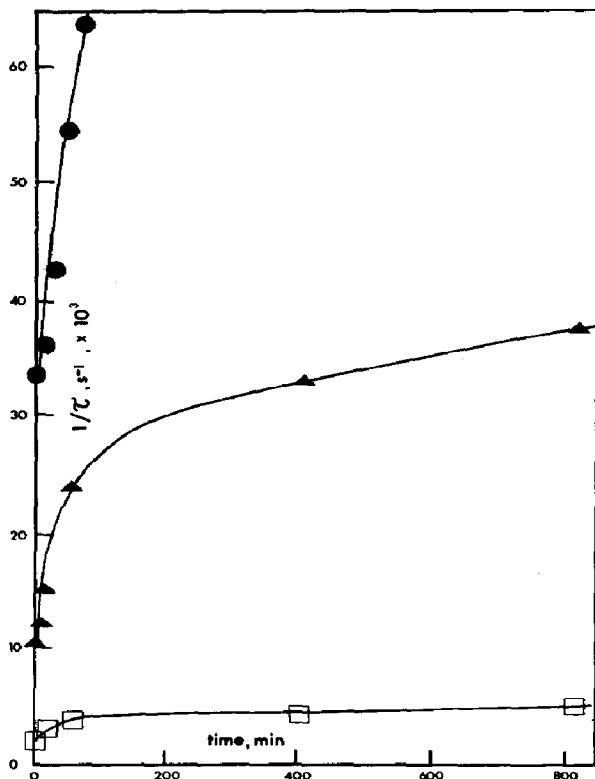


Fig. 3. The effect of irradiation on the inverse triplet lifetime for $\lambda_{\text{irr}} > 400 \text{ nm}$ and $[(\text{CH}_3\text{CO})_2] = 12.6 \times 10^{-4} \text{ mol l}^{-1}$: □, 101 °C; ▲, 146 °C; ●, 177 °C.

Here B represents a ground state molecule, ${}^3\text{B}_n$ is a triplet biacetyl molecule in an upper vibrational level, and ${}^1\text{B}_0$ and ${}^3\text{B}_0$ are vibrationally equilibrated singlet and triplet states respectively.

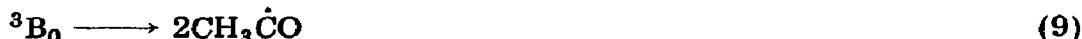
Excitation of biacetyl at 440 nm generates the first excited singlet state 1A_u of biacetyl with virtually no excess vibrational energy [14, 15]. Since for the ground state molecule about 70 kcal mol⁻¹ is necessary to rupture the weakest bond ($\text{CH}_3\text{CO})_2 \rightarrow 2\text{CH}_3\dot{\text{C}}\text{O}$), absorption of 440 nm radiation (65 kcal mol⁻¹) will not decompose biacetyl directly. Intersystem crossing in biacetyl singlets is the dominant, if not the exclusive, relaxation mode other than fluorescence in the gas phase [12, 16]. Thus, except for a small amount of fluorescence ($\phi_f \approx 2.5 \times 10^{-3}$ [13]), excitation into low-lying levels of the first singlet state results in 100% conversion into the corresponding triplet state 3A_u . Even at the lowest concentration studied in this work vibrational relaxation of the triplet can be assumed to be complete before the onset of phosphorescence. Consequently the present results are concerned with the kinetics of thermalized triplet molecules.

The observed independence of the triplet lifetime at 25 °C on biacetyl concentration in the range $2.5 \times 10^{-5} - 1.35 \times 10^{-3} \text{ mol l}^{-1}$ supports the view of previous workers [12, 17] that self-quenching (reaction (8)) is

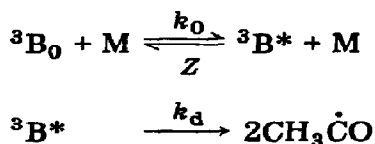
negligible. The average of all the data for concentrations which exclude diffusional effects gives $1/\tau = k_6 + k_7 = (5.71 \pm 0.20) \times 10^2 \text{ s}^{-1}$. This result is in excellent agreement with the lifetime reported in the literature [13, 17] for triplet biacetyl vapour excited using light of wavelengths near 440 nm, *i.e.* $1/\tau = (5.3 - 6.7) \times 10^2 \text{ s}^{-1}$.

The phosphorescence lifetime was found to be strongly temperature dependent, the decay rate for the triplet state increasing with temperature. The rate constants k_6 , for radiative decay, and k_7 , for intersystem crossing from the triplet state to the ground electronic state, can be assumed to be almost independent of temperature [18, 19]. Hence some additional reaction channel must become important at higher reaction temperatures to account for the observed increase in triplet decay rate. Similar results have been reported from studies on the primary photochemical yield for biacetyl vapour excited at 435.8 nm. A first order dissociation process has been observed [8] at temperatures in excess of 100 °C and the data has been shown to be consistent with a mechanism involving unimolecular dissociation of the triplet state with an activation energy of about 15 kcal mol⁻¹.

Reaction (9) is added to the mechanism to account for the photochemical behaviour in the gaseous phase:



The lifetime data obtained in this study show no concentration effect for temperatures up to 123 °C (Table 1). However, the biacetyl phosphorescence lifetimes were strongly concentration dependent at higher temperatures. The usual Stern–Volmer plots of $1/\tau$ versus concentration were non-linear, with the decay rate approaching a maximum value which was insensitive to further increases in concentration (Fig. 1). Thus the results suggest that self-quenching (reaction (8)) must be unimportant over the complete temperature range studied (25 - 189 °C) and the inverse triplet lifetime at elevated temperatures is given by $1/\tau = k_6 + k_7 + k_9$. The inverse triplet lifetime versus concentration plots show an increasing degree of curvature with increasing temperature and are similar to those found for unimolecular rate constant fall-off curves. A concentration-dependent decomposition in competition with phosphorescence would produce just the kind of behaviour observed and it is concluded that the curvatures of the Stern–Volmer plots result from the concentration dependence of the decomposition of the triplet state biacetyl molecules. The decomposition pathway (reaction (9)) may be written in terms of the following simple scheme:



where k_0 , Z and k_d are the specific rate constants for second order collisional activation, for collisional deactivation of energized molecules ${}^3\text{B}^*$ and for spontaneous decomposition of collisionally energized molecules respectively.

Steady state treatment of the above scheme gives the following simple Hinshelwood–Lindemann relationship for the experimentally observed unimolecular rate constant k_g (obs):

$$k_g \text{ (obs)} = k_0 k_d / Z (1 + k_d / Z [M])^{-1}$$

The lifetime data in Table 1 and Fig. 1 can be used to evaluate the Arrhenius parameters for both the triplet decomposition rate constant k_∞ ($= k_0 k_d / Z$) in the high pressure limit and the rate constant k_0 in the low pressure limit. The lifetime data for temperatures up to 123 °C were independent of concentration and give directly the high pressure limiting rate constants k_∞ . At higher temperatures k_∞ was determined from the limiting maximum value of the observed lifetime in the presence of high concentrations of carbon dioxide. The rate constant k_0 for second order collisional activation was obtained from the slope of a plot of $1/k_g$ (obs) against the reciprocal of the biacetyl concentration (Fig. 4). The values of k_∞ and k_0 derived at each temperature are shown plotted in Arrhenius form in Figs. 5 and 6 respectively and yield

$$k_\infty = 10^{11.3 \pm 0.5} \exp \{-(13.9 \pm 0.8 \text{ kcal mol}^{-1})/RT\} \text{ s}^{-1}$$

and

$$k_0 = 10^{12.4 \pm 0.5} \exp \{-(7.6 \pm 1.0 \text{ kcal mol}^{-1})/RT\} \text{ l mol}^{-1} \text{ s}^{-1}$$

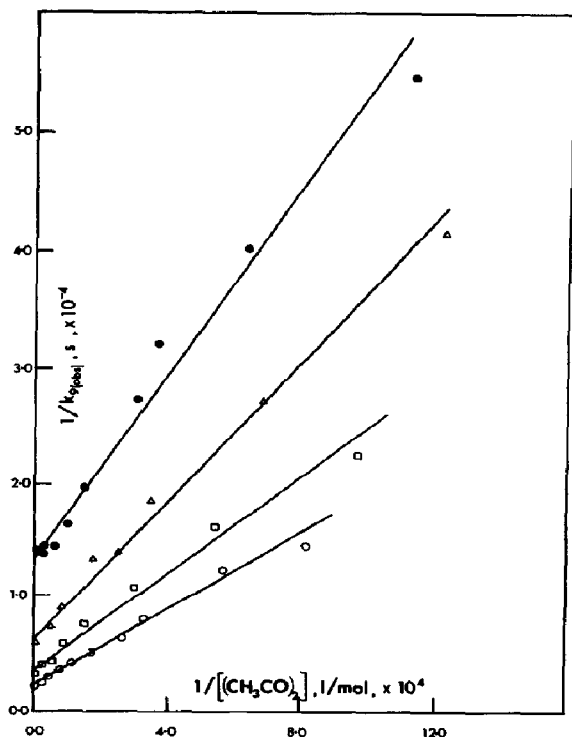


Fig. 4. Hinshelwood–Lindemann plots of $1/k_g$ (obs) vs. the reciprocal of the biacetyl concentration: ●, 144 °C; ▲, 161 °C; □, 177 °C; ○, 189 °C.

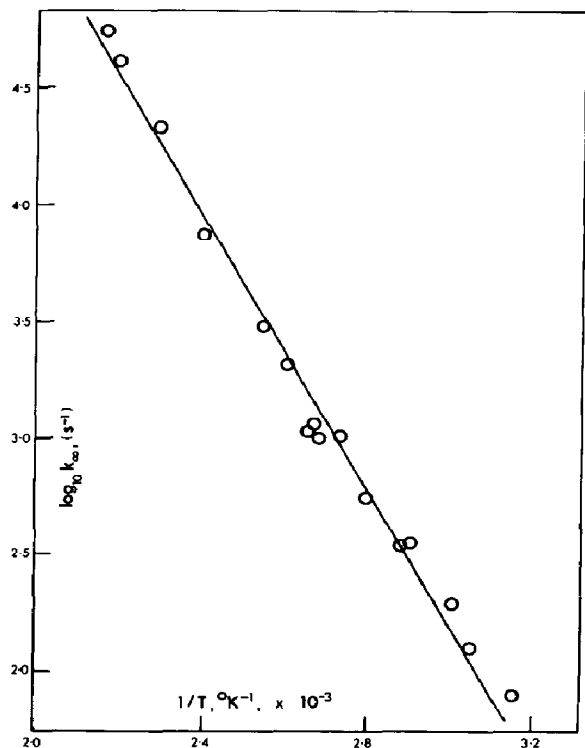


Fig. 5. An Arrhenius plot of the high pressure limiting rate constant for the decomposition of the triplet state of biacetyl.

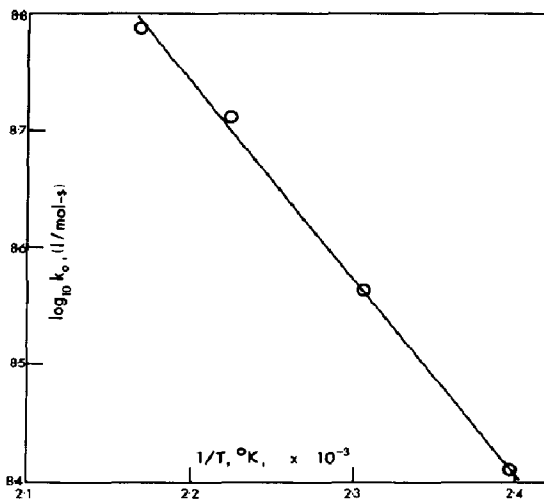


Fig. 6. An Arrhenius plot of the second order collisional activation rate constant for the decomposition of the triplet state of biacetyl.

The high pressure limiting activation energy is in excellent agreement with that estimated from the photochemical decomposition studies of Noyes *et al.* [8]. The pre-exponential factor for the triplet photocleavage of the central bond is somewhat lower than is generally found for simple bond fission processes. However, a low A factor might be expected since there is a lack of electronic state correlation between the 3A_u triplet state of biacetyl and the ground state photoproducts [20, 21].

Previous determinations of the gas phase Arrhenius parameters for the unimolecular α cleavage of triplet state carbonyl compounds are relatively scarce and somewhat conflicting. O'Neal and Larson [18] have estimated an activation energy of $9.6 \text{ kcal mol}^{-1}$ and an A factor of $10^{10.1} \text{ s}^{-1}$ for the photodecomposition of acetone triplets. In contrast, Abuin and Lissi [22] have reported an activation energy of $12.7 \text{ kcal mol}^{-1}$ with an A factor of $10^{14.6} \text{ s}^{-1}$ for the structurally similar butan-2-one triplet state.

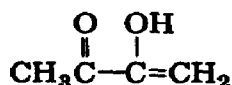
The number s of effective oscillators in the energized triplet biacetyl molecule may be estimated from the expression [23]

$$E_\infty - E_0 = \frac{1}{2}(s - 1)RT$$

At the mean temperature of the experiments described in this work (166.5 °C) $E_{\infty} - E_0 = 6.3 \text{ kcal mol}^{-1}$ corresponds to 15 effective oscillators, compared with a total of 30 vibrational modes. This result is in line with the value of $s = 13$ for the decomposition of the triplet state of acetone (24 vibrational modes), calculated from the data of O'Neal and Larson [18] at 38 °C.

The decrease in triplet lifetime with increasing temperature is in qualitative agreement with the decrease in the overall phosphorescence quantum yield over this temperature range [4]. However, a contributing factor to the reduction in emission yield could be a decrease in the production of triplets from the singlet state. At 25 °C intersystem crossing from the singlet state to the triplet state occurs with near unit efficiency [12, 16]. However, it is possible that some alternative decay path for the singlet state may become important at higher temperatures. The relative initial intensity I_p^0 of phosphorescence is directly proportional to the concentration of triplets formed by intersystem crossing from the singlet state. Since, under the experimental conditions used, the triplet decay is negligible compared with their rate of formation, no measurable decay can occur before the phosphorescence intensity observations begin. The ratio I_p^0/I_0 given in the last column of Table 2 is directly proportional to the quantum yield of triplet formation and is found to be constant, within experimental error, over the temperature range 25 - 119 °C. This result indicates that the singlet state decay processes are relatively independent of temperature and it provides support for the observation [3, 4] that the quantum yield of fluorescence is independent of temperature. Unfortunately no temperature dependence lifetime studies have been reported for the singlet state.

The results shown in Fig. 3 indicate that some reaction product produced during continuous photolysis of biacetyl at wavelengths greater than 400 nm quenches the triplet state of biacetyl extremely efficiently. The major products detected following photolysis of biacetyl under these conditions are CO, C₂H₆, CH₂CO, CH₃CHO and CH₃COCH₃ [9]. However, triplet quenching rate data for these species suggest that they are relatively inefficient quenchers and the concentrations produced during the photolysis experiments in this work are considerably below those required to account for the high level of triplet state quenching. It must therefore be concluded that some undetected product is responsible for the increased triplet decay rate and that this product must be extremely efficient in quenching the triplet state. Various workers [9, 10] have found that some product of the photolysis of biacetyl has a very strong absorption at 275 nm and have suggested that it is due to the enolic form of biacetyl, *i.e.* to



Certainly the position and high extinction coefficient of this absorption band are consistent with a $\pi^* \leftarrow \pi$ absorption of a conjugated unsaturated

carbonyl system, and a similar photochemically induced enolization has been reported [24] for *ortho*-substituted benzophenones. The mechanism for enol formation probably involves an internal hydrogen abstraction process which takes place through a highly strained four-membered transition state. The high quenching efficiency of the enol structure is presumably the result of a triplet-triplet energy transfer reaction. For the reaction to be rapid, the enol structure would be required to have a triplet state several kilocalories per mole below that for the normal dione-structured triplet state.

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