

TEMPERATURE EFFECTS ON THE QUENCHING OF THE TRIPLET STATE 3A_u OF BIACETYL

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Summary

Rate data for the quenching of the triplet state 3A_u of biacetyl were determined for a number of collision partners in the gas phase as a function of temperature. Quenching by oxygen and nitric oxide resulted in negative temperature coefficients and the results were interpreted on the basis of the formation of collision complexes. The Arrhenius parameters determined for the reaction of triplet biacetyl molecules with acetaldehyde are an indication that the n,π^* configuration of biacetyl behaves like a biradical in the gas phase. The results are consistent with a hydrogen atom abstraction reaction channel.

1. Introduction

The triplet n,π^* excited electronic states of carbonyl-containing compounds undergo a large number of important photochemical and photophysical processes [1 - 3]. For instance the ability of the triplet states of ketones to abstract hydrogen from suitable substrates is thought to be a critical step in ketone photoreduction. Also quenching of electronically excited triplet molecules by the paramagnetic species oxygen and nitric oxide has been shown to be particularly efficient. However, the kinetic interpretation of these photochemical quenching experiments has normally been derived from rate data obtained at room temperature.

Recently the lifetime of the triplet state of biacetyl has been determined as a function of temperature [4]. As a consequence it is now possible to obtain rate data for the quenching of the triplet state over a range of temperatures. Quenching of the triplet state of biacetyl by known hydrogen atom donors in solution is well documented [5] and it has been suggested that alkyl alcohols [6] and amines [7] quench the triplet state in the vapour phase by hydrogen atom transfer. In common with many other ketones the phosphorescence emission from biacetyl has been shown to be effectively quenched by both oxygen [8] and nitric oxide [9, 10].

This work is concerned with the gas phase collisional quenching of triplet 3A_u biacetyl by oxygen, nitric oxide and acetaldehyde over a relatively wide temperature range utilizing time-resolved laser-excited phosphorescence. The rate constants derived should be of value in the interpretation of the quenching mechanisms.

2. Experimental

Triplet 3A_u biacetyl molecules were generated from the first excited singlet state 1A_u by intersystem crossing. The experimental arrangement was similar to that described previously [4]. A 500 ns pulse of laser light at 440 nm was used to excite biacetyl to its first excited singlet state close to the 0-0 band of the $^1A_u \leftarrow ^1A_g$ transition. Neutral density filters were used to reduce the intensity of the laser beam to about 2 μ J per pulse in order to ensure that triplet-triplet annihilation reactions were unimportant [11]. The T-shaped Pyrex luminescence cell was housed in an insulated air furnace which was temperature controlled to better than ± 0.2 °C. Phosphorescence from excited biacetyl molecules was detected in a direction perpendicular to the incident laser beam using an EMI 9659QB photomultiplier fitted with a 500 nm long-pass filter. The photomultiplier output was fed into a Tektronix model 549 oscilloscope and the trace displayed was photographed. The decays were single exponentials and the lifetimes were determined with a reproducibility of better than 3%.

A greaseless mercury-free vacuum system was used for all the experiments. Pressure measurements were made using a mercury manometer coupled to a Pyrex spiral gauge. Biacetyl was purified as previously described [4]. Carbon dioxide, oxygen and nitric oxide were research grade gases from Matheson Gas Products. Acetaldehyde (BDH) with a stated purity of greater than 99% was trap-to-trap distilled on the vacuum line with the middle fraction being retained and stored under liquid nitrogen. The middle fraction was found to contain no impurities when analysed by gas-liquid chromatography.

3. Results and discussion

The triplet state lifetime of biacetyl was determined as a function of temperature for the various collision partners with added concentrations of quenchers in the range 2×10^{-5} - 6×10^{-3} mol l $^{-1}$. At temperatures in excess of 120 °C the lifetime of pure biacetyl has been shown to be concentration dependent [4]. The concentration dependence exists because the unimolecular decomposition of triplet biacetyl occurs in the fall-off region. To avoid complications arising from this fall-off behaviour, quenching experiments at elevated temperatures were always carried out in the presence of carbon dioxide as an inert diluent. This ensured that the rate of decom-

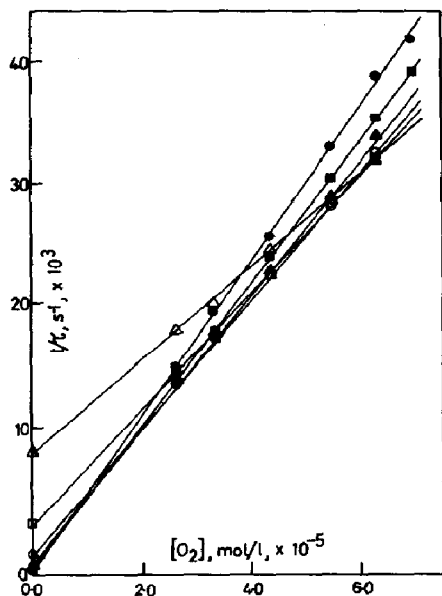


Fig. 1. Stern-Volmer plots of the inverse biacetyl triplet lifetime against the concentration of oxygen: ●, 25 °C; ■, 50 °C; ▲, 75 °C; ○, 100 °C; □, 120 °C; △, 140 °C.

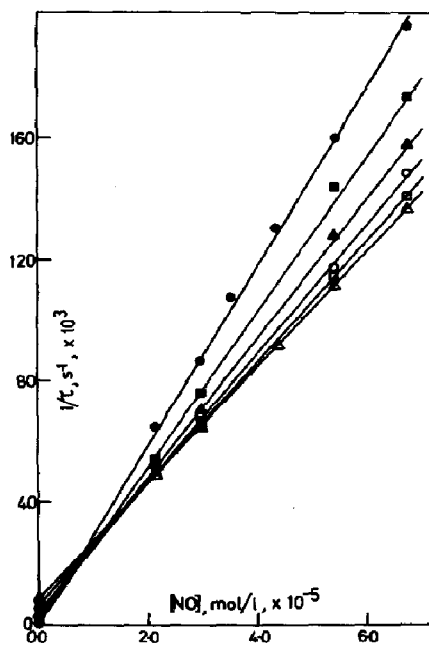


Fig. 2. Stern-Volmer plots of the inverse biacetyl triplet lifetime against the concentration of nitric oxide: ●, 25 °C; ■, 50 °C; ▲, 75 °C; ○, 100 °C; □, 120 °C; △, 140 °C.

position of triplet biacetyl was in the limiting first-order region and that changes in the observed lifetime were purely a function of the reaction between triplet biacetyl and the added quencher. The lifetime for a given quencher concentration was independent of the biacetyl concentration ($5 \times 10^{-5} - 1.5 \times 10^{-3} \text{ mol l}^{-1}$) which confirms that biacetyl self-quenching is negligible [4, 12]. Lifetimes of a particular sample were measured during the heating cycle and were then remeasured at a low temperature to confirm that quenching by decomposition products did not interfere.

The following mechanism adequately accounts for the reactions of triplet biacetyl in the presence of quenching molecules.



Reaction sequence (1) contains all the photophysical processes preceding the formation of vibrationally relaxed triplet molecules 3B_0 . In terms of this mechanism the inverse triplet lifetime of biacetyl is given by

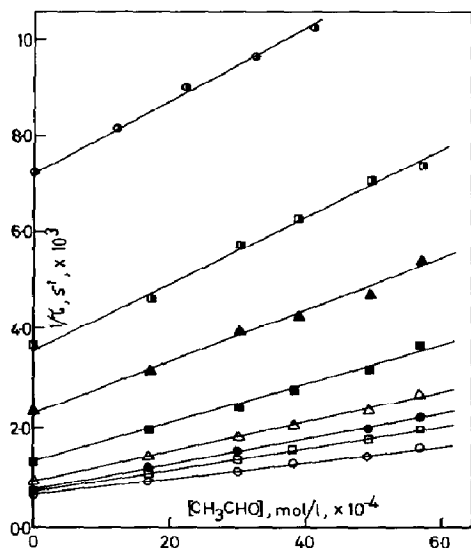


Fig. 3. Stern-Volmer plots of the inverse biacetyl triplet lifetime against the concentration of acetaldehyde: ○, 25 °C; □, 44 °C; ●, 61 °C; △, 84 °C; ■, 99 °C; ▲, 112 °C; ◻, 123 °C; ●, 142 °C.

$$1/\tau = k_2 + k_3 + k_4 + k_5[Q]$$

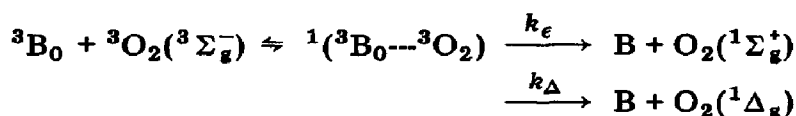
Plots of the inverse triplet lifetime against the concentration of added quencher were linear for each of the gases investigated (Figs. 1 - 3). Stern-Volmer analyses of the data allowed estimates of the quenching rate constants (Table 1) to be made.

The quenching rate constants determined for oxygen and nitric oxide at 25 °C are in excellent agreement with the values previously reported by Calvert and coworkers [8, 9]. The rate constant for quenching of triplet biacetyl by oxygen decreases slightly with increasing temperature and gives rise to an apparent small negative activation energy of 384 cal mol⁻¹. The lifetime observed for a biacetyl-oxygen mixture was insensitive to the further addition of high concentrations of carbon dioxide (up to 2.5 × 10⁻² mol l⁻¹). Hence the negative temperature coefficient is not due to a third-body dependence in the system. The mechanism for quenching the n,π* triplet state of biacetyl may be either physical or chemical in nature. Electronic energy transfer, leading to excitation of oxygen from its ground state to one of its low-lying singlet states, is expected to be a significant removal pathway. Intermolecular enhancement of spin-forbidden triplet state decay by molecular oxygen is thought to result from an electronic interaction between the triplet state and an oxygen molecule within a collision complex [13, 14]. The details of the kinetics of the quenching process can be analysed according to the following scheme in which the overall spin is conserved.

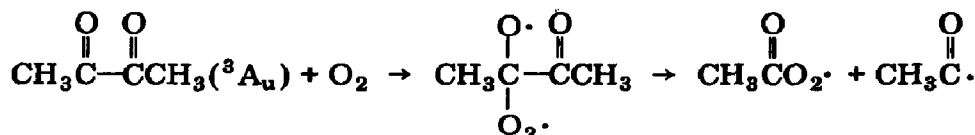
TABLE 1

Quenching rate constant data for biacetyl triplet molecules with various collision partners as a function of temperature

Collision partner	Temperature (°C)	Quenching rate constant (l mol ⁻¹ s ⁻¹)
Oxygen	25	(5.66 ± 0.27) × 10 ⁸
	50	(5.44 ± 0.31) × 10 ⁸
	75	(5.34 ± 0.37) × 10 ⁸
	100	(4.75 ± 0.32) × 10 ⁸
	120	(5.15 ± 0.38) × 10 ⁸
	140	(4.65 ± 0.45) × 10 ⁸
Nitric oxide	25	(2.81 ± 0.10) × 10 ⁹
	50	(2.47 ± 0.33) × 10 ⁹
	75	(2.15 ± 0.29) × 10 ⁹
	100	(1.99 ± 0.23) × 10 ⁹
	120	(1.99 ± 0.18) × 10 ⁹
	140	(1.89 ± 0.13) × 10 ⁹
Acetaldehyde	25	(1.80 ± 0.17) × 10 ⁵
	44	(2.64 ± 0.45) × 10 ⁵
	61	(2.73 ± 0.55) × 10 ⁵
	84	(2.87 ± 0.33) × 10 ⁵
	99	(4.11 ± 0.57) × 10 ⁵
	112	(4.79 ± 0.34) × 10 ⁵
	123	(7.00 ± 0.67) × 10 ⁵
	142	(7.24 ± 0.50) × 10 ⁵



where ${}^1({}^3\text{B}_0\cdots{}^3\text{O}_2)$ denotes a collision complex in a singlet state. The results indicate that the stability of the collision complex decreases with temperature and that the rate of decomposition of the complex back to the triplet state is important at higher temperatures. It is also possible that interaction of the triplet state with oxygen could lead directly to chemical changes in the system. Photolysis of biacetyl-oxygen mixtures at 435.8 nm in the gas phase yields carbon dioxide, carbon monoxide, water, methanol and formaldehyde as products [15 - 17]. From a detailed study on this system Padnos and Noyes [17] concluded that product formation arises from the reaction of oxygen with the triplet state presumably by the reaction



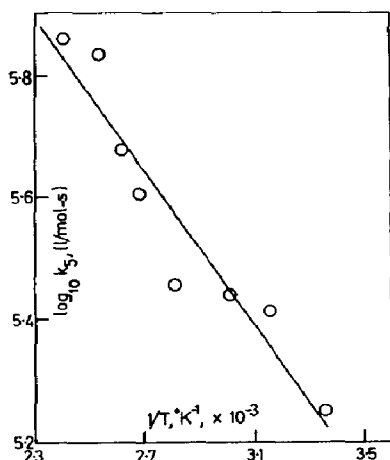
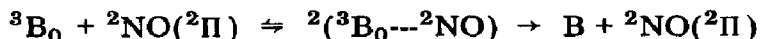


Fig. 4. An Arrhenius plot of the quenching rate constant for the biacetyl triplet state by acetaldehyde.

The mean values of the quantum yields were $-\phi_{O_2} = 0.27$, $\phi_{CO_2} = 0.15$ and $\phi_{CO} = 0.04$ although there was considerable experimental scatter in the results. Excitation into low-lying levels of the first singlet results in virtually 100% conversion into the triplet state [8] and thus the quantum yield data refer directly to the reaction of the triplet state with molecular oxygen. Without a complete mechanism for the photooxidation process it is impossible to estimate quantitatively the importance of the direct chemical quenching reaction relative to the energy transfer process from these quantum yields. However, the relatively low values for $-\phi_{O_2}$ and ϕ_{CO_2} are an indication that energy transfer is the dominant reaction channel.

Quenching of triplet biacetyl by nitric oxide has features similar to those found in the oxygen quenching studies. Thus quenching by nitric oxide resulted in a negative temperature coefficient with an apparent activation energy of $-851 \text{ cal mol}^{-1}$ and quenching rate constants that were independent of the total reactant concentration. An energy transfer pathway can be unambiguously ruled out on energetic grounds for nitric oxide since the energy of the lowest lying available state ($^4\Pi$) lies about $100 \text{ kcal mol}^{-1}$ above the ground state. Gijzeman *et al.* [18] have proposed that quenching of excited triplet states by nitric oxide involves the formation of a spin-allowed doublet collision complex.

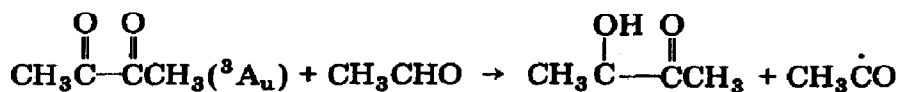


Decomposition of the triplet-doublet biacetyl-nitric oxide collision complex at higher temperatures would account for the observed negative temperature coefficient.

An Arrhenius plot of the rate data determined for the quenching of biacetyl triplets by acetaldehyde is shown in Fig. 4 and gives

$$k_{5(CH_3CHO)} = 10^{7.3 \pm 0.5} \exp\{-(2.9 \pm 0.6 \text{ kcal mol}^{-1})/RT\} \text{ l mol}^{-1} \text{ s}^{-1}$$

The pre-exponential factor is in the range found for free radical hydrogen atom abstraction reactions and an activation energy of $2.9 \text{ kcal mol}^{-1}$ is consistent with a hydrogen atom abstraction process involving a relatively weak C—H bond ($D(\text{H—COCH}_3) = 86 \text{ kcal mol}^{-1}$ [19]). Hence the rate parameters are an indication that the n, π^* configuration of biacetyl behaves like a biradical in the gas phase.



It is of interest to compare the present results with those reported for the reaction of hydroxyl and methoxy radicals with acetaldehyde. Atkinson and Pitts [20] have studied the reaction of hydroxyl radicals with acetaldehyde over the temperature range $26 - 154 \text{ }^\circ\text{C}$ and report a rate constant for hydrogen abstraction of $k = 10^{9.6} \exp\{-(-0.5 \text{ kcal mol}^{-1})/RT\} \text{ l mol}^{-1} \text{ s}^{-1}$. Kelly and Heicklen [21] report a value of $k = 1.1 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ at $25 \text{ }^\circ\text{C}$ for the analogous reaction of methoxy radicals. Assuming a value of $A = 10^{8.0} \text{ l mol}^{-1} \text{ s}^{-1}$ for the pre-exponential factor for this reaction a value of $1.3 \text{ kcal mol}^{-1}$ may be estimated for the activation energy. The relatively high activation energy observed for hydrogen atom abstraction from acetaldehyde is presumably because of resonance stabilization in the excited state, which makes the reaction less thermodynamically favourable than the analogous hydroxyl and methoxy radical reactions.

The biradical behaviour of triplet biacetyl in solution has been the subject of considerable attention. Reaction with isopropyl alcohol [5, 22, 23], benzhydrol [24] and tri-*n*-butyl stannane [5] results in efficient photo-reduction of biacetyl. When biacetyl is irradiated in isopropyl alcohol, pinacol and acetone are formed in essentially quantitative yield [22]. With benzhydrol both benzophenone and pinacol were observed as products [24] and for tri-*n*-butyl stannane pinacol was again detected [5]. Thus the available evidence is an indication that these molecules quench the biacetyl triplet by hydrogen atom donation to yield the biacetyl ketyl radical. The presence of the ketyl radical has been confirmed in irradiated solutions of biacetyl by electron paramagnetic resonance [25, 26].

The Arrhenius parameters obtained in this work for acetaldehyde quenching are an indication that the reaction of triplet biacetyl with hydrogen atom donors in the gas phase also involves an abstraction process.

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