QUENCHING OF THE TRIPLET STATE ^3A_u OF BIACETYL BY HALOGENATED COMPOUNDS

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Summary

The lifetime of excited triplet ^3A_u biacetyl molecules was determined in the presence of various halogenated methanes and hydrogen halides. Stern—Volmer analysis of the data gave the following quenching rate constants in the gas phase at 25 °C (in units of litres per mole per second): CF_4, less than 5×10^2; CF_3Cl, 1.9×10^5; CF_3Br, 5.0×10^5; CF_3I, 9.3×10^6; CCl_3Br, 8.2×10^5; CH_4, less than 5×10^2; CH_3Cl, 1.0×10^4; CH_3Br, 3.7×10^4; CH_3I, 4.2×10^5; HCl, 5.1×10^5; HBr, 2.7×10^7. The quenching rate constants observed for the halogenated methanes are consistent with a halogen atom abstraction process. The data for the hydrogen halides are interpreted in terms of a mechanism involving hydrogen atom abstraction with the formation of the biacetyl ketyl radical.

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1. Introduction

Bimolecular quenching reactions of the $n\pi^*$ triplet state of the α-dicarbonyl biacetyl have been reported for a variety of chemical species. Efficient intermolecular triplet electronic energy transfer has been demonstrated [1] for molecules possessing lower triplet energy levels than biacetyl. However, quenching is much less efficient for molecules with higher triplet energies and it appears that the endothermicity plays a significant role [1, 2]. The ability of other compounds to quench the triplet state of biacetyl can be rationalized in terms of mechanisms involving direct chemical reaction. Alkyl alcohols and amines are thought to quench the triplet state in the vapour phase by hydrogen atom transfer [3, 4] and quenching by known hydrogen atom donors in solution is well documented [5]. Recently Carr and Ramirez [3] have investigated the effect of alkyl iodides on the phosphorescence emission from biacetyl. Their data indicate that quenching by the iodides occurs via a chemical pathway and it has been suggested that reaction with the iodine could be responsible. Similarly the high quenching efficiency observed with molecular iodine [6] probably results from some

rapid chemical reaction with the triplet state. There is little experimental data available for quenching by other halogen-containing molecules. Addition of up to 400 Torr of hexafluoroethane had no measurable influence on the quantum yield of biacetyl phosphorescence [7] and is probably a consequence of the chemical inertness of C—F bonds. However, Garabedian and Dows [8] have found that appreciable quenching of phosphorescence from biacetyl occurs in the presence of methyl chloride.

The present work is concerned with the gas phase collisional quenching of the triplet state ^3A_u of biacetyl by a number of halomethanes and hydrogen halides. It was hoped that the results would provide information on the mechanisms of the reactions which lead to removal of the triplet state.

2. Experimental

Biacetyl was excited to its first excited singlet state with a flashlamp-pumped tunable dye laser (Electrophotonics Ltd., Model 23). The laser was tuned to enable excitation at 440 nm with a bandwidth of 1 nm using Coumarin 2 as the laser dye. The laser output was attenuated with neutral density filters to provide an approximately 2 μJ pulse of about 500 ns duration. The T-shaped Pyrex emission cell of path length 10 cm was temperature controlled in an isothermal oven. All experiments were carried out at 25.0 ± 0.2 °C. The emission was monitored at right angles to the laser beam using an E.M.I. 9659QB photomultiplier. A Corning CS3-69 filter transmitting light of wavelengths greater than 500 nm was positioned in front of the photomultiplier tube housing to discriminate against fluorescence emission and scattered laser light. The phosphorescence signal was recorded on a Tektronix model 549 oscilloscope and was photographed using a Polaroid camera. All the phosphorescence decays observed were single exponential in character and lifetimes were determined with reproducibilities to within better than 3%.

The gaseous mixtures were prepared in a conventional mercury-free greaseless vacuum system using a Pyrex spiral manometer as a null instrument for pressure measurement. A thermal gradient pump in series with the cell was used to mix the reactants.

The biacetyl (Fluka, Puriss) had a stated purity of 99.5% and was degassed and distilled under vacuum with retention of the middle boiling fraction. Methyl iodide (E. Merck AG, Darmstadt) and trifluoromethyl iodide (Fluorochem Ltd.) were purified by treatment with sodium thiosulphate solution. The resulting reagents were dried, were degassed under vacuum and were stored in the dark at −196 K. Bromotrichloromethane (Aldrich) was purified by preparative gas chromatography prior to use. All other reagents were from Matheson Gas Products and were purified by trap-to-trap distillation on the vacuum line. Before each experiment the biacetyl-quencher mixtures were thoroughly degassed in order to ensure the elimination of molecular oxygen.

3. Results and discussion

The behaviour of biacetyl (B) following excitation at 440 nm in the presence of an added gas (Q) can be rationalized in terms of the following mechanism [9, 10] :

$$B + h\nu \quad \rightarrow {}^1B_0 \rightarrow {}^3B_n \overset{M}{\rightarrow} {}^3B_0 \tag{1}$$

$$^3B_0 \quad \rightarrow B + h\nu_p \tag{2}$$

$$^3B_0 \quad \rightarrow B \tag{3}$$

$$^3B_0 + Q \rightarrow B + Q \tag{4}$$

$$^3B_0 + Q \rightarrow B + {}^3Q \tag{5}$$

$$^3B_0 + Q \rightarrow products \tag{6}$$

Wall deactivation is unimportant at the relatively high pressures used in these experiments [11] and the low light intensities employed preclude any significant contribution to triplet removal from triplet–triplet annihilation [12]. This mechanism leads to the following expression for the observed triplet lifetime in the presence of an added quencher:

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

where $k_Q = k_4 + k_5 + k_6$.

Stern–Volmer plots of the quenching data for each gas were linear, as is required by this equation (Figs. 1 - 3). The slopes provide estimates of k_Q
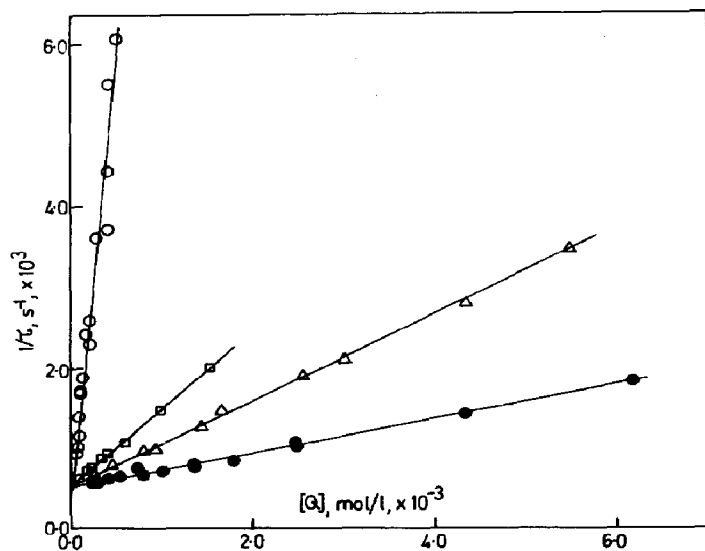

Fig. 1. Stern–Volmer plots of the inverse biacetyl triplet lifetime *vs.* the concentration of added halogenated methane: ○, CF_3I; □, CCl_3Br; △, CF_3Br; ●, CF_3Cl.
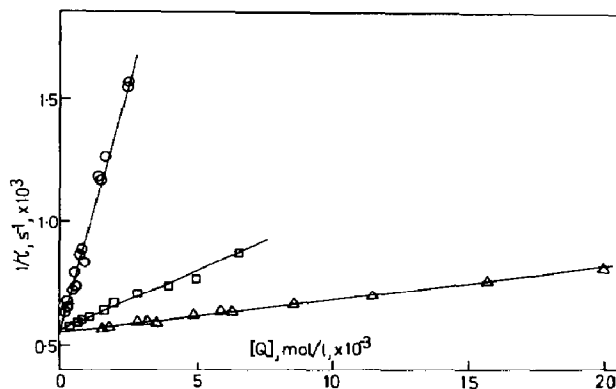
Fig. 2. Stern—Volmer plots of the inverse biacetyl triplet lifetime $vs.$ the concentration of added methyl halide: $\bigcirc$, CH_3I; $\square$, CH_3Br; $\triangle$, CH_3Cl.
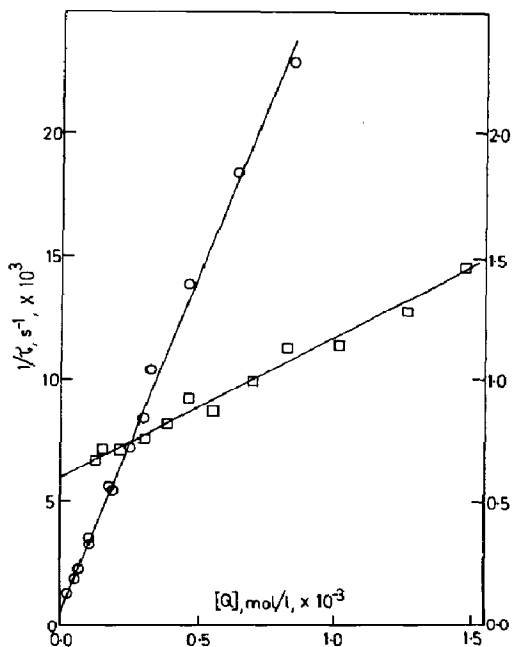
Fig. 3. Stern—Volmer plots of the inverse biacetyl triplet lifetime $vs.$ the concentration of added hydrogen halide: $\bigcirc$, HBr, left-hand scale; $\square$, HCl, right-hand scale.

for the various halogenated compounds studied (Table 1). Mixtures of biacetyl and the quenching gases were left in the reaction cell in the dark for approximately 24 h. The lifetimes were found to be unchanged and it was concluded that dark reactions are unimportant. Since biacetyl self-quenching is negligible [10, 14], the lifetime of a particular biacetyl–quencher mixture is expected to be independent of the biacetyl pressure. This was confirmed in experiments for each added gas studied for biacetyl pressures in the range from 1 to 25 Torr.

Jackson and Yarwood [15] have concluded from a detailed study of the effect of high pressures of xenon on phosphorescence emission from biacetyl that collisionally induced intersystem crossing from the triplet state to the ground state via the external heavy atom effect is negligible. This observation supports the proposal of Vanquickenborne and McGlynn [16] that external heavy atom effects are small for $n\pi^*$ carbonyl triplets. Thus the observed collisional quenching by the various halogenated compounds must involve either energy transfer, reaction (5), or direct chemical reaction of the quenching molecule with the triplet state, reaction (6).

The first absorption band of the halogenated methanes is continuous in nature and corresponds to the n → σ^* singlet transition [17]. The halogenated methanes studied in this work have absorption maxima in the region 170 - 270 nm. Although no evidence has been found for the direct popula-

TABLE 1

Quenching rate constant data for biacetyl triplet molecules with various halogenated compounds at 25 °C

Quencher	$D(R-X)$[a] (kcal mol^{-1})	Quenching rate constant k_Q (l mol^{-1} s^{-1})
CF$_3$—F	130	$<5 \times 10^2$
CF$_3$—Cl	86	$(1.92 \pm 0.08) \times 10^5$
CF$_3$—Br	71	$(4.99 \pm 0.07) \times 10^5$
CF$_3$—I	54	$(9.30 \pm 0.08) \times 10^6$
CCl$_3$—Br	55	$(8.19 \pm 0.34) \times 10^5$
CH$_3$—H	104	$<5 \times 10^2$
CH$_3$—Cl	84	$(1.01 \pm 0.06) \times 10^4$
		4.9×10^4 [b]
CH$_3$—Br	70	$(3.66 \pm 0.26) \times 10^4$
CH$_3$—I	56	$(4.17 \pm 0.15) \times 10^5$
		$(1.0 \pm 0.2) \times 10^6$ [c]
H—Cl	103	$(5.05 \pm 0.35) \times 10^5$
H—Br	87	$(2.74 \pm 0.06) \times 10^7$

[a] Data taken from ref. 13.
[b] Data taken from ref. 8.
[c] Data taken from ref. 3.

tion of the corresponding triplet state, this forbidden band would be expected to occur towards only slightly longer wavelengths than those for the allowed transition. Since the 0—0 band of the $^1A_g \rightarrow {}^3A_u$ transition of biacetyl occurs at 502 nm [10] (57 kcal mol^{-1}), energy transfer to the triplet state of the halogenated methanes would be highly endothermic. Thus quenching by an energy transfer channel is expected to be negligible.

The quenching reactions of the halogenated methanes appear to be consistent with some form of halogen atom abstraction process and probably involve the carbon atom of the electronically excited carbonyl system. There is a progressive increase in the quenching rate constant for the trifluoromethyl halide series in going from CF$_4$ to CF$_3$I. This trend is in accordance with the decrease in the C—halogen bond strength. The small rate constant for CF$_4$ quenching reflects the chemical inertness of C—F bonds. A similar trend is evident for the methyl halide series where quenching by CH$_3$I is significantly more efficient than quenching by CH$_3$Cl. The low reactivity of methane suggests that the C—H bonds in the methyl halides are unreactive and that quenching arises from attack at the halogen atom.

Comparison of the data for the methyl and trifluoromethyl halide series shows that the quenching rate for a trifluoromethyl halide is at least an order of magnitude faster than that for the corresponding methyl compound. This is unexpected in terms of bond dissociation energy criteria since there is very little difference between the C—halogen bond strength of a methyl halide and that of the trifluoromethyl analogue. The increase in reactivity of CF$_3$I over CH$_3$I, for example, can be explained in terms of polar effects. When a

radical or radical-like centre abstracts a halogen atom there will be considerable repulsion between the odd electron of the radical and the closed shell of the halogen atom. The repulsion should be reduced if an electron-attracting group is bonded to the halogen atom. The $n\pi*$ electronic state configuration of carbonyl species is thought to be radical like and electrophilic in the region of the half-filled n orbital on oxygen and is thought to be nucleophilic above and below the carbonyl faces because of the presence of an electron in the $\pi*$ orbital [18]. The increase in the quenching rate for the trifluoromethyl halides can be ascribed to a reduction in the electron density on the abstracted halogen atom. As a consequence, attack of the nucleophilic carbon atom of the $n\pi*$ triplet state of biacetyl will be considerably enhanced relative to attack on the corresponding methyl halide.

The C—Br bond dissociation energy in CCl_3Br is some 15 - 16 kcal mol^{-1} weaker than that in CF_3Br or CH_3Br, and quenching of the triplet state of biacetyl was found to be more efficient. However, the effect of the reduction in bond strength in going from CF_3Br to CCl_3Br appears to be counterbalanced to some extent by increased polar forces. In contrast, the increase in reactivity of CCl_3Br over CH_3Br can be ascribed to a combination of reduced bond dissociation energy and reduced polar repulsions.

The results obtained for the quenching of the triplet state of biacetyl by HBr and HCl are consistent with a hydrogen atom abstraction process involving the oxygen atom of the $n\pi*$ carbonyl system:

$$CH_3COCOCH_3\ (^3A_u) + HX \rightarrow CH_3\overset{\overset{\displaystyle OH}{|}}{C}COCH_3 + X\cdot$$

The relative magnitudes of the quenching rate constants for HBr and HCl suggest that the bond energy of the H—X bond being broken is an important factor in the reaction. Larson and O'Neal [19] have found that quenching of the acetone triplet state by HBr is very efficient with $k_Q = 6.3 \times 10^8$ l mol^{-1} s^{-1} at 25 °C. Their results from phosphorescence quenching and product analysis experiments indicate that the quenching reaction involves hydrogen atom abstraction from HBr by the acetone triplet state. The lower quenching rate observed with triplet biacetyl probably results from the lower triplet energy of triplet biacetyl relative to that of acetone. This would cause the hydrogen atom abstraction step to become relatively more endothermic.

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