

PHOSPHORESCENCE QUENCHING OF BIACETYL VAPOR BY ALCOHOLS AND IODIDES*

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Summary

The quenching of phosphorescence emission from biacetyl, excited at 404.7 nm, has been investigated in the gas phase for several alcohols and iodides. The data gave linear Stern–Volmer plots, from which quenching rate constants for collisions of 3B_u biacetyl were determined. The rate constant values in l/mol s were: methyl alcohol (7.6×10^5), ethyl alcohol (6.2×10^5), n-propyl alcohol (7.2×10^5), methyl iodide (1.0×10^6), ethyl iodide (1.1×10^6), n-propyl iodide (6.7×10^5), and methylene iodide (2.9×10^6).

Using simple hard sphere collision theory, the collisional efficiencies of quenching, per gas kinetic collision, were all in the range 2 to 5×10^{-6} , except for methylene iodide, which was 1.4×10^{-5} . The quenching mechanism for the alcohols is most probably H-atom transfer from the alcohol to 3B_u biacetyl. For the iodides, the data cannot be used to distinguish unambiguously between an external heavy atom effect and chemical quenching.

Introduction

The phosphorescence of biacetyl vapor can be quenched by bimolecular collisions of the emitting state with a wide variety of different chemical species. The diatomic molecules oxygen [1 - 5], nitric oxide [4, 6], and iodine [7] are efficient quenchers. Also, the polyatomic molecules azomethane [6], azoethane [6] and anthracene [8] are highly efficient quenchers, requiring only a few gas kinetic collisions to deactivate triplet biacetyl molecules by exothermic triplet–triplet energy transfer. Polyatomic species which have higher triplet energy levels than biacetyl quench with much lower efficiency, and at least in some cases by mechanisms other than triplet–triplet transfer. Alkyl amines are thought to quench by H atom transfer in the vapor phase [9], and in the liquid phase alcohols have been shown to quench by H transfer [10]. Of the alcohols, only isopropyl alcohol appears to have been

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investigated in the gas phase [11]. In addition to triplet-triplet energy transfer and chemical reaction, a third quenching mechanism which has been investigated is the external heavy atom effect. External heavy atom effects on $n-\pi^*$ triplet states are thought to be small [12]. Garabedian and Dows [11] found no evidence for such an effect in phosphorescence quenching of biacetyl by methyl chloride, but there are conflicting reports on the interaction of xenon with triplet biacetyl [13, 14]. In connection with this, the efficient quenching by iodine [7] noted above could be due to either an external heavy atom effect or to chemical reaction.

We have investigated the bimolecular quenching of biacetyl phosphorescence by a series of alkyl iodides (methyl iodide, ethyl iodide, n-propyl iodide, and methylene iodide) and a series of aliphatic alcohols (methyl alcohol, ethyl alcohol and n-propyl alcohol). The iodides were of interest to see if, in view of the high quenching efficiency of iodine, the alkyl iodides would also quench biacetyl phosphorescence efficiently. We also chose to study the alcohols since apart from isopropyl alcohol, no study of biacetyl quenching by these species has been reported.

Experimental

Apparatus

A conventional 10^{-6} Torr Pyrex vacuum apparatus was used. Radiation from an Osram HBO 500 W Hg arc was passed through a Bausch and Lomb High Intensity grating monochromator with entrance and exit slits set to pass a 5 nm band centered at 404.7 nm. The emergent radiation was collimated and passed longitudinally through a T-shaped Pyrex vessel, 5 cm long and 2.5 cm in diameter, having Suprasil windows. Emission was viewed at a right angle to the cell by a 0.5 m grating spectrometer equipped with a 1P28 photomultiplier.

Materials

Aldrich research grade biacetyl was degassed by vacuum pumping at -78°C , and stored also at this temperature. Fisher reagent grade methyl alcohol, ethyl alcohol and n-propyl alcohol were dried with anhydrous CaSO_4 , followed by degassing at -78°C before storage at -196°C . The methyl iodide and ethyl iodide were Aldrich research grade chemicals, n-propyl iodide and methylene iodide were Eastman reagent grade. Repeated washings with 0.1 N aqueous $\text{Na}_2\text{S}_2\text{O}_3$ were followed by drying over CaSO_4 . The washed product absorption spectrum, measured on a Beckman DK-1 spectrophotometer, indicated the disappearance of the 478 nm I_2 absorption band. The purified iodides were degassed under vacuum before storing in the dark at -196 K .

Procedure

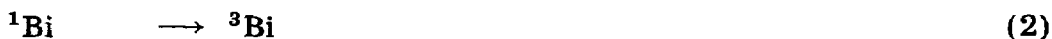
All experiments were done at room temperature, $(22 \pm 2^\circ\text{C})$. The foreign gas (0 - 8 mm) was introduced into the T-cell, and 25 mm of biacetyl

was next expanded into the cell. After complete mixing, the emission intensity was recorded in arbitrary units, and the mixture was discarded. Phosphorescence intensity measurements were taken at 510 nm. Small corrections for background radiation (<1%) and fluorescence emission (~1%) were made to the observed signal.

Results and discussion

Mechanism and rate constants

The primary photochemical process in biacetyl excited at 404.7 nm, where it does not decompose may be adequately represented by the following simplified kinetic scheme [15]:



In step (1), biacetyl, Bi, is raised to the first excited singlet state, ${}^1\text{Bi}$, from which it may fluoresce (3), or intersystem cross (2) to the triplet manifold, ${}^3\text{Bi}$. The triplet state, ${}^3\text{Bi}$, may phosphoresce (4), intersystem cross to the ground state (5), or be collisionally deactivated by either Bi [3, 8] or added foreign gases. A steady-state analysis of ${}^1\text{Bi}$ and ${}^3\text{Bi}$ yields eqn. (7) for the ratio of phosphorescence intensity, I_p , to absorbed intensity, I_a , in pure biacetyl:

$$I_p/I_a = \frac{k_4}{k_4 + k_5 + k'_6 [\text{Bi}]} \quad (7)$$

With a foreign gas present, a similar equation can be written.

$$I_{pM}/I_a = \frac{k_4}{k_4 + k_5 + k'_6 [\text{Bi}] + k_6 [\text{M}]} \quad (8)$$

For constant biacetyl pressure, and hence constant I_a , the ratio of eqn. (7) to eqn. (8) yields:

$$\frac{I_p}{I_{pM}} = 1 + \frac{k_6 [\text{M}]}{k_4 + k_5 + k'_6 [\text{Bi}]} \quad (9)$$

Equation (9) predicts that a plot of I_p/I_{pM} vs. $[\text{M}]$ should be a straight line with unit intercept. Figures 1 and 2 are plots of the data for the alcohols and iodides. Table 1 contains the least squares values of the slopes, obtained from Figs. 1 and 2, along with the standard deviation. Also in Table 1 are the ratios of the slopes, normalized to CH_2I_2 , which are the relative quenching rate constants.

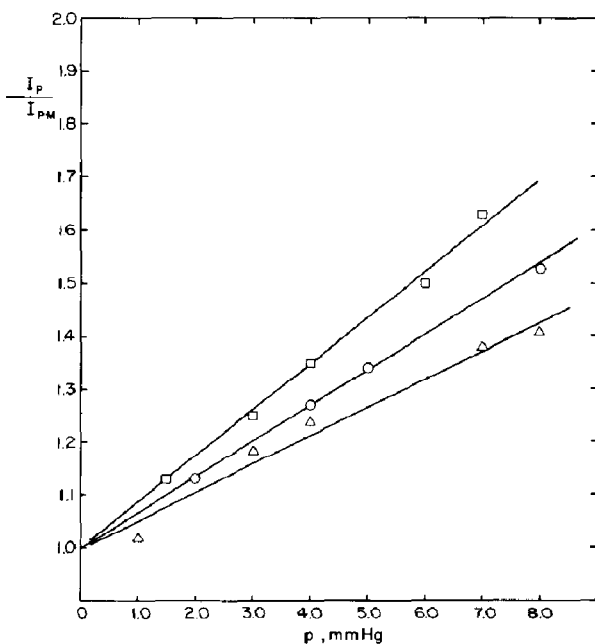


Fig. 1. Plot of phosphorescence intensity of pure biacetyl to phosphorescence intensity in the presence of a foreign gas, I_p/I_{pM} , versus foreign gas pressure. ○, CH₃OH; △, C₂H₅OH; □, CH₃I. Biacetyl pressure, 25 Torr; $T = 22 \pm 2^\circ\text{C}$; $\lambda_{\text{ex}} = 404.7 \text{ nm}$.

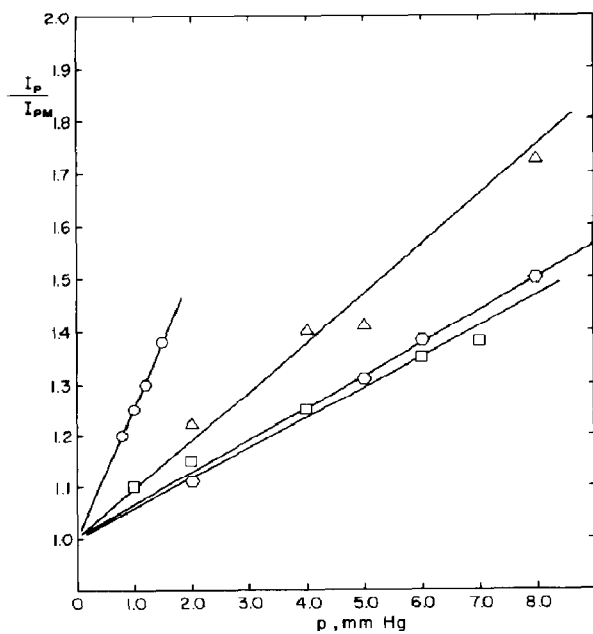


Fig. 2. Plot of phosphorescence intensity of pure biacetyl to phosphorescence intensity in the presence of a foreign gas, I_p/I_{pM} , versus foreign gas pressure. ○, CH₂I₂; △, C₂H₅I; □, n-C₃H₇I; ○, n-C₃H₇OH. Biacetyl pressure 25 Torr; $T = 22 \pm 2^\circ\text{C}$, $\lambda_{\text{ex}} = 404.7 \text{ nm}$.

TABLE 1

Gas	$\frac{k_6}{k_4 + k_5 + k'_6 [\text{Bi}]}$ (mm^{-1})	Quenching efficiency	k_6 (l/mol s)	$\eta_{\text{Bi},M}$	$Z_{\text{Bi},M} \times 10^{-11}$ l/mol s)
CH_3OH	$(6.33 \pm 0.32) \times 10^{-2}$	0.26	$(7.6 \pm 0.4) \times 10^5$	2.83×10^{-6}	2.69
$\text{C}_2\text{H}_5\text{OH}$	$(5.14 \pm 1.16) \times 10^{-2}$	0.21	$(6.2 \pm 1.4) \times 10^5$	2.33×10^{-6}	2.66
n- $\text{C}_3\text{H}_7\text{OH}$	$(5.97 \pm 0.48) \times 10^{-2}$	0.24	$(7.2 \pm 0.6) \times 10^5$	2.74×10^{-6}	2.63
CH_3I	$(8.55 \pm 1.71) \times 10^{-2}$	0.35	$(1.0 \pm 0.2) \times 10^6$	4.9×10^{-6}	2.04
$\text{C}_2\text{H}_5\text{I}$	$(8.98 \pm 3.83) \times 10^{-2}$	0.37	$(1.1 \pm 0.5) \times 10^6$	5.12×10^{-6}	2.15
n- $\text{C}_3\text{H}_7\text{I}$	$(5.51 \pm 1.65) \times 10^{-2}$	0.23	$(6.7 \pm 2.0) \times 10^5$	2.98×10^{-6}	2.25
CH_2I_2	$(2.44 \pm 0.12) \times 10^{-1}$	1.0	$(2.9 \pm 0.1) \times 10^6$	1.39×10^{-5}	2.09

Sidebottom *et al.* [3] have reported $k_4 = (1.0 \pm 0.2) \times 10^2 \text{ s}^{-1}$, $k_5 = (5.6 \pm 1.3) \times 10^2 \text{ s}^{-1}$ and $k'_6 = 4 \times 10^3 \text{ l/mol s}$ at 25 °C. Using these rate coefficients, the values of k_6 reported in Table 1 were calculated. Finally, if k_6 is assumed to be expressible as the product of a gas kinetic collision number and a collision efficiency, $k_6 = Z_{\text{Bi},\text{M}}\eta_{\text{Bi},\text{M}}$, the collision efficiencies reported in Table 1 could be calculated. The collision numbers were calculated from simple hard-sphere collision theory. The molecular diameters were: biacetyl, 6.81 Å [11]; CH₃OH, 3.69 Å [16]; C₂H₅OH, 4.31 Å [16]; n-C₃H₇OH, 4.71 Å [16]; CH₃I, 4.45 Å [17]; C₂H₅I, 4.84 Å [17]; n-C₃H₇I [17], 5.20 Å; CH₂I₂, 5.15 Å [17].

According to the mechanism given by reactions (1) - (9), all of the changes in phosphorescence intensity which we have observed are due to collisions of the biacetyl triplet with added alkyl iodide or alcohol. Consideration of some other mechanistic possibilities shows them to be unimportant. Collision-induced S₁ → T intersystem crossing can at most make a very small contribution to the phosphorescence intensity since (1) all of the initially excited ¹A_u biacetyl molecules that do not fluoresce ($\Phi_f = 0.0025$ [18]) undergo an intramolecular radiationless transition to the ³A₄ state [19], and (2) a comparison of the first order total relaxation rate constant of the ¹A_u state with the collision frequency at 35 Torr reveals that 1 out of every 3 - 4 collisions of the ¹A_u state with added alkyl iodide or alcohol (at 10 Torr of additive) would have to be effective in promoting S₁ → T intersystem crossing to make it equal the first order relaxation rate. Quenching by oxygen, present as an impurity, also seems highly unlikely. For oxygen quenching, which has a rate constant equal to $5.2 \times 10^8 \text{ l/mol s}$ [3], to equal the observed quenching for a quencher having a rate constant equal to $6 \times 10^5 \text{ l/mol s}$ which is typical of the lowest values observed in this work, would require an oxygen impurity of 0.1%. The careful degassing procedures and vacuum techniques used preclude such high oxygen levels. Finally, wall quenching will be unimportant for the cell dimensions and at the pressures used in this work [4].

Although the triplet energies of the alcohols and iodides used in this study are not well known, reasonable estimates place them at least 50 kcal/mol and 25 kcal/mol higher than the 56 kcal/mol triplet energy of biacetyl. Thus quenching *via* triplet-triplet electronic energy transfer, eqn. (10), would have to be a highly endothermic process:



A crude estimate of k_{10} can be obtained from an Arrhenius equation, $k_{10} = Z_{\text{Bi},\text{M}} \exp(-\Delta E_T/RT)$. Taking $Z_{\text{Bi},\text{M}}$ to be $2 \times 10^{11} \text{ l/mol s}$, (see Table 1) and the difference in triplet energy levels, ΔE_T , to be 25 kcal/mol yields $k_{10} = 1.2 \times 10^{-7} \text{ l/mol s}$. Thus the electronic energy transfer mechanism falls far short of explaining the data.

The most likely mechanism for quenching by the alcohols is H atom transfer to biacetyl. Work in liquid solutions has shown that quenching of biacetyl phosphorescence by known hydrogen donors occurs, and products

that can be attributed to H atom transfer have been identified [10]. The bimolecular rate constants for CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and $n\text{-C}_3\text{H}_7\text{OH}$ (Table 1), are somewhat larger than, for example, cyclohexane [3] (3.4×10^3 l/mol s) and propylene [11] (6×10^4 l/mol s), but similar to dimethylamine [9] (3×10^5 l/mol s) and diethylamine [9] (6.2×10^5), where quenching by H atom transfer has also been suggested to occur.

Fuller, Phillips and Almy [7] observed that addition of 0.007 mm of iodine to 49 mm of biacetyl reduced the emission to less than 3% of its intensity in the absence of iodine. The effective quenching cross-section for iodine was stated to be 50 - 100 times greater than for quenching by oxygen. The quenching efficiencies of the alkyl iodides are considerably lower than this. For example, 1.5 mm of methyl iodide reduces the emission intensity by about 30%. The high efficiency of iodine is presumably not due to an external heavy atom effect, in view of the rather low quenching ability of xenon [13, 14], and the theoretical expectation [12] of small effects on triplet n, π^* states. This leads to the conclusion that iodine quenches biacetyl phosphorescence by reaction with $^3\text{B}_\eta$ biacetyl. The high reactivity of iodine towards species with unpaired spins is well known.

Whether the alkyl iodides quench biacetyl by chemical reaction or by an external heavy atom effect cannot be unambiguously determined from the present data. Heavy atoms can enhance absorption from the ground electronic state to the first excited triplet state, the rate constants of the radiationless processes to and from the triplet state, and the rate constant of phosphorescence [20]. The experimental findings have been controversial concerning the relative effects of external heavy atoms on radiative and radiationless processes [20], *i.e.*, whether the rate of radiative transitions is promoted to a greater or lesser extent than the rate of radiationless transitions. Recently, Grabowski and Sadlej [21] found that radiative and radiationless deactivation of triplet *p*-phenylbenzophenone and *p*-methoxyacetophenone in rigid glasses containing ethyl bromide or ethyl iodide are influenced to a similar extent by the external heavy atoms.

As mentioned above, a negligible effect is expected on $\text{S}_1 \rightarrow \text{T}$ intersystem crossing in biacetyl, and at the pressures used in this work. Consequently, any heavy atom effect would have to be exerted upon $\text{T} \rightarrow \text{S}_0$ intersystem crossing and upon phosphorescence. To explain the results, the external heavy atom effect upon the radiationless transition would have to be larger than on the radiative transition. A more attractive possibility is that the iodides quench biacetyl by chemical reaction, perhaps by reaction with the iodine. This is consistent with the fact that methylene iodide is the most reactive of those studied, and *n*-propyl iodide is the least reactive.

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