Vapor-Phase Bimolecular Quenching of the Triplet State of Biacetyl

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Abstract: A study of the pressure dependence of the phosphorescence of biacetyl vapor has demonstrated that a bimolecular quenching of the lowest triplet state occurs. The quenching rate constants for collisions with biacetyl, acetone, methyl chloride, propylene, and isopropyl alcohol have been determined at 25°. The efficiency of the quenching collisions was found to be of the order of 10^{-6} for all of the gases studied.

For the past 25 years biacetyl has received attention because of its phosphorescence in the gas, liquid, and solid phases. Because of its relatively low triplet-state energy (about 20,000 cm^{-1}), biacetyl has been used extensively in triplet energy-transfer studies.

In 1943 Almy and Gillette[2] measured the quantum yield of biacetyl phosphorescence at 5100 Å produced by 4047- and 4358-Å excitation. They cite a value of 0.145 ± 0.03, approximately independent of pressure. Later studies by Okabe and Noyes[3a] and Heicklen[3b] again failed to demonstrate any pressure dependence of the phosphorescence quantum yield. This pressure independence has been taken to indicate the absence of appreciable bimolecular quenching of the phosphorescing triplet.

Because of the wide use of biacetyl in studying energy-transfer processes, we have further investigated the bimolecular aspects of the phosphorescence by carrying out a study of the pressure dependence of the intensity, both in pure biacetyl and in mixtures with other gases. We have used a Stern–Volmer approach to obtain information on the quenching efficiencies.

Theory and Mechanism

At the exciting wavelength employed, principally 4000 ± 150 Å, biacetyl is raised to its first excited singlet state on absorption of a photon. The singlet molecule can then cross to the first excited triplet state, or it can return to the ground state *via* fluorescence or internal conversion. From the triplet state the molecule may return to the ground state by phosphorescence or internal conversion, or during a collision. The following mechanism is postulated for initial consideration (an asterisk indicates vibrational excitation).

$$h\nu + \text{Bi} \longrightarrow {}^1\text{Bi}^* \tag{1}$$

$$^1\text{Bi}^*\,(+\text{M}) \longrightarrow {}^1\text{B}\,(+\text{M}) \tag{2}$$

$$^1\text{Bi}\,(+\text{M}) \longrightarrow \text{Bi}\,(+\text{M}) \tag{3}$$

$$^1\text{Bi} \longrightarrow \text{Bi} + h\nu_\text{F} \tag{4}$$

$$^1\text{Bi} \longrightarrow {}^3\text{Bi}^* \tag{5}$$

$$^3\text{Bi}^*\,(+\text{M}) \longrightarrow {}^3\text{Bi}\,(+\text{M}) \tag{6}$$

$$^3\text{Bi} \longrightarrow \text{Bi} \tag{7}$$

$$^3\text{Bi} \longrightarrow \text{Bi} + h\nu_\text{P} \tag{8}$$

$$^3\text{Bi} + \text{M} \longrightarrow \text{Bi} + \text{M} \tag{9}$$

Several justifiable assumptions may now be made which simplify the mechanism which must be considered. All indications are that ^{1}Bi either fluoresces or forms ^{3}Bi;[4] thus step 3 may be neglected. Since the ratio of phosphorescence to fluorescence yield is about 60:1,[3a] step 4 may be neglected. Vibrational relaxation is very efficient,[5,6] and thus steps 2 and 6 are rapid compared to other processes. In effect these assumptions imply that every act of absorption leads to a triplet biacetyl molecule in its ground vibrational state.

Decomposition was negligible since no 3650-Å radiation was allowed to reach the cell and because the quantum yield for photodissociation at 4000 Å is very small.[7]

These assumptions allow a simplified mechanism to be written.

$$h\nu + \text{Bi} \longrightarrow {}^3\text{Bi} \tag{a}$$

$$^3\text{Bi} \longrightarrow \text{Bi} + h\nu_\text{P} \tag{b}$$

$$^3\text{Bi} \longrightarrow \text{Bi} \tag{c}$$

$$^3\text{Bi} + \text{Bi} \longrightarrow \text{Bi} + \text{Bi} \tag{d}$$

$$^3\text{Bi} + \text{M} \longrightarrow \text{Bi} + \text{M} \tag{d'}$$

The intensity of phosphorescence (I_P) is then

$$I_\text{P} = k_\text{b}(^3\text{Bi}) \tag{10}$$

Steady-state considerations for (^{3}Bi) yield

$$I_\text{P} = \frac{k_\text{b}k_\text{a}\Delta I}{k_\text{b} + k_\text{c} + k_\text{d}'(\text{M}) + k_\text{d}(\text{Bi})} \tag{11}$$

where ΔI is the light absorbed in the region seen by the phosphorescence detector. Explicit account has been taken of biacetyl (k_d) as a quencher in addition to M (k_d') in eq 9. In the experiment a beam of light of intensity I_0 falls on the cell. After passage through a window and through 10 cm of the gas sample, the beam reaches the center of the observation section (I_D at point D = 10 cm). The beam then proceeds through another 10 cm of sample and another window and is detected (I_T). The intensity at the center of the observation point is $I_\text{D} = I_0(I_\text{T}/I_0)^{1/2}$. Absorption in the short (about 2 cm) observation section is linear under the conditions of the experiment to much better than

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[1] Taken from a dissertation submitted by M. E. G. in partial fulfillment of the requirements for the Ph.D. degree.

[2] G. M. Almy and P. R. Gillette, *J. Chem. Phys.*, **11**, 188 (1943).

[3] (a) H. Okabe and W. A. Noyes, *J. Amer. Chem. Soc.*, **79**, 810 (1957); (b) J. Heicklen, *ibid.*, **81**, 3863 (1959).

[4] T. Backstrom and J. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

[5] S. H. Bauer, *Ann. Rev. Phys. Chem.*, **16**, 245 (1965).

[6] D. W. Setser, B. S. Rabinovitch, and J. W. Simons, *J. Chem. Phys.*, 40, 1751 (1964).

[7] W. A. Noyes, G. B. Porter, and J. E. Jolley, *Chem. Rev.*, **56**, 49 (1956).

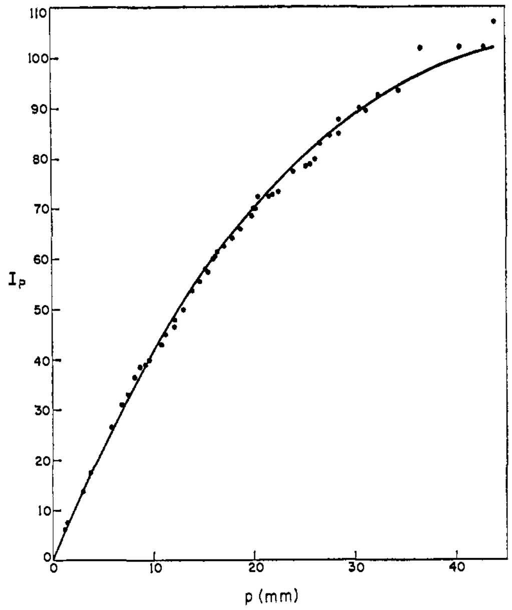

Figure 1. Intensity of biacetyl phosphorescence (arbitrary units) *vs.* pressure in pure gaseous biacetyl at 25°. The solid line is computed from the final experimental parameters k and α (eq 11).

1%. Thus ΔI is proportional to $I_0(I_T/I_0)^{1/2}p$, where p is the biacetyl pressure.[8]

Taking the reciprocal of eq 11 and substituting for ΔI

$$\text{constant} \times \frac{P}{I_P}\left(\frac{I_T}{I_0}\right)^{1/2} = \frac{k_b + k_c}{k_b k_a I_0} + \frac{k_d'(M) + k_d(Bi)}{k_b k_a I_0} \qquad (12)$$

In the case of pure biacetyl, a plot of the left-hand side of eq 12 against pressure of biacetyl should yield a straight line of slope $s = k_d/k_b k_a I_0$ and an intercept $i = (k_b + k_c)k_b k_a I_0$. The ratio $s/i = k_d/(k_b + k_c)$.

In the case of an added gas, an analogous plot of the left-hand side of eq 12 against the pressure of added gas should yield $k_d'/(k_b + k_c)$. An alternate plot of $(I_P)_{M=0}/(I_P)_M$ *vs.* the pressure p_M of the added gas should yield an intercept of unity and a slope $k_d'/(k_b + k_c + k_d p)$, where p is again the biacetyl pressure.

Experimental Section

The biacetyl (or biacetyl–foreign gas mixture using one of the gases acetone, propylene, isopropyl alcohol, or methyl chloride) was placed in a cell in the form of a cross, with phosphorescence observed at right angles to the exciting light beam. This cell was enclosed in a light-tight box which also housed, in compartments, the photomultiplier detector and filters. Light from a BH-4 mercury lamp was passed through a series of filters which isolated the region of the 4047-Å mercury line. The filtered light then passed through the sample gas cell as an approximately parallel beam. An RCA 931A photomultiplier monitored the transmitted beam. A second photomultiplier accepted the green phosphorescence from the cross-arm of the cell, after the light had passed through an interference filter which transmitted a 200-Å band centered at 5100 Å. The signals were measured using an Eldorado Model 210 photometer. Scattered light was slight and was corrected for, as were the small changes in incident light intensity.

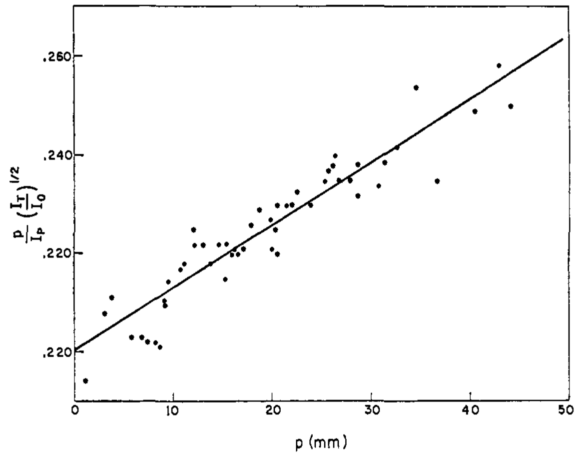

Figure 2. Stern–Volmer plot of biacetyl phosphorescence corrected for absorption of incident light.

Chemicals used were reagent grade liquids or gases, degassed and distilled under vacuum at least twice. Particular care was taken to remove oxygen from the samples, since oxygen is an efficient quencher for triplet biacetyl.[9] The test for absence of oxygen was a reproducible maximum intensity (in a single experiment and between experiments using different samples prepared on different days) after repeated freezing and degassing of the sample.

Errors in the phosphorescence intensity due to all sources of error are estimated to be a maximum of 3% at the lowest pressures studied. Gases were handled on a conventional glass vacuum system equipped with a glass Bourdon gauge to measure pressures to an accuracy of 0.2 mm. There was no temperature effect on I_P when the environment of the cell was warmed from 24 to 42°.

In Figure 1 the observed phosphorescence intensities (arbitrary units) are plotted against pressure for pure biacetyl. The data for this plot were taken on several occasions and in several sequences of pressure change. It is evident that there is considerable departure from linear behavior of intensity as the pressure is increased. Figure 2 shows a plot of the left-hand side of eq 12 against the pressure of biacetyl, and, apart from the scatter of points, the linear behavior predicted is observed. A least-squares fit of the data yields a line (shown on the figure) with slope 0.00129 ± 0.00027 mm^{-1} and an intercept 0.200 ± 0.006 (standard deviations of the parameters are given). The ratio of these quantities gives $k_d/(k_b + k_c) = 0.0065 \pm 0.0013$ mm^{-1}.

In order to determine the quenching constants for the added gases, plots of the left-hand side of eq 12 and/or of $(I_P)_{M=0}/(I_P)_M$ *vs.* p_M were made as discussed above. Such plots yield values of $k_d'/(k_b + k_c)$, which are listed in Table I. By writing k_d in terms of a collision frequency Z and a quenching efficiency η ($k_d' = Z_{Bi-M}\eta_{Bi-M}$), it is possible to derive quenching efficiencies for the added gases relative to biacetyl itself, since in taking ratios the factor $k_b + k_c$ (always the *biacetyl* unimolecular rate) cancels. The molecular diameters, σ (Å), involved in the calculation of Z were taken from molecular models: biacetyl, 6.81; acetone, 5.37, propylene, 5.33; isopropyl alcohol, 5.17; and methyl chloride, 2.87. The relative efficiencies are also listed in Table I.

Table I. Ratio of the Bimolecular Quenching Constant to the Unimolecular Deactivation Rate Constant of Triplet Biacetyl, and Relative Quenching Efficiencies of Various Gases

Gas	$k_d/(k_b + k_c)$, mm^{-1}	η'/η
Biacetyl	$(6.5 \pm 1.3) \times 10^{-3}$	1.00
Acetone	$(3.9 \pm 0.5) \times 10^{-3}$	0.64 ± 0.2
Propylene	$(5.7 \pm 0.6) \times 10^{-3}$	0.84 ± 0.3
Isopropyl alcohol	$(4.1 \pm 0.4) \times 10^{-3}$	0.71 ± 0.2
Methyl chloride	$(4.4 \pm 0.5) \times 10^{-3}$	1.10 ± 0.3

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(8) ΔI is also proportional to $\alpha p I_0 \exp(-\alpha p D)$, where α, the absorption coefficient, is $(1.17 \pm 0.09) \times 10^{-3}$ cm^{-1} mm^{-1} (corresponding to $\epsilon = 10.2$ l./(mole cm)) as determined in this work. The absorption coefficient was tested and found to be independent of added gas pressure with the gases used. In the pressure range studied, ΔI is quite nonlinear in p.

(9) W. E. Kaskan and A. B. F. Duncan, *J. Chem. Phys.*, **18**, 427 (1950).

Discussion

Two comments may be made immediately concerning the data of Table I, where the quenching efficiencies of the five gases are all approximately equal. First, all the added gases have their lowest triplet states higher in energy than does biacetyl. Thus none of the molecules are expected to show the high-efficiency quenching expected when downhill triplet–triplet energy transfer is possible, and, in fact, none do show a high efficiency. Methyl chloride was chosen as one of the added gases in part to check for a possible heavy-atom effect in enhancing triplet–singlet crossing; no such effect made itself evident.

Second, consideration was given to the possibility that hydrogen abstraction might be important as a quenching mechanism, as observed by Walling and Gibian in the case of benzophenone.[10] Even though the C–H bond energies vary by 10–18 kcal in the quenching molecules, there is no great difference in the relative quenching efficiencies.

The lifetime of the triplet state of biacetyl has been measured.[11,12] In the absence of quenching the unimolecular constant ($k_b + k_c$) which appears in the data of Table I is simply the reciprocal of the lifetime; $k_b + k_c = 1/(1.7 \times 10^{-3}$ sec). The more recent determination[11] was carried out on a sample consisting of a low pressure of biacetyl in 20 mm of benzene vapor. If benzene has a quenching effect similar to that of the added gases of this experiment, the true value of $k_b + k_c$ will have a value about 10% smaller than above, or about 5.3×10^2 sec^{-1}. Using this value the rate constants k_d (biacetyl) and k_d' (added gases) have been calculated, and they are presented (in more common units) in Table II. Also given in Table II are effective collision cross sections ($\pi\sigma^2$) and collision efficiencies (η).

Conclusion

It has been demonstrated that the biacetyl triplet state is appreciably quenched by a number of gases. Previous workers[2,3] have noted the approximate independence of phosphorescence intensity with pressure, but their data sometimes show a slight slope in Stern–Stern–Volmer-type plots. For instance, Coward and Noyes[13] show (their Figure 1) a slight slope, which is consistent to within the errors involved with these results. The work of Almy and Gillette,[2] on which all statements concerning the phosphorescence quantum yield of biacetyl are based, was carried out in the pressure range 0–50 mm of biacetyl. On the average over this range quenching decreases the phosphorescence yield by about 16%, and their result for the quantum yield should be increased from 0.143 to about 0.17 to apply at zero pressure. This change is just within the error of 0.03 which they quote.

Table II. Bimolecular Quenching Rate Constants, Effective Collision Cross Sections, and Collision Efficiencies for Quenching of the Triplet State of Biacetyl at 25°

Quenching gas	$k_d{}^a \times 10^{16}$	$\pi\sigma^{2b} \times 10^{21}$	$\eta \times 10^6$
Biacetyl	1.18	3.0	0.22
Acetone	0.71	1.7	0.14
Propylene	1.0	2.1	0.18
Isopropyl alcohol	0.74	1.7	0.16
Methyl chloride	0.80	1.8	0.24

[a] Units of molecule^{-1} sec^{-1} cm^3; rate constant for eq d or d′. [b] In cm^2.

In solution in typical organic solvents the diffusion-limited rate for bimolecular reactions is of the order 10^{10} l./(mole sec). If this rate is taken as limiting the flow of excitation energy away from a quenched biacetyl molecule, the efficiency, η, approximately 10^{-7}, suggests an upper limit of 10^3 l./(mole sec) for the quenching of biacetyl by a solvent similar to the molecules used as added gases in this study. In the pure solvent (plus dilute biacetyl) a triplet biacetyl lifetime of the order 10^{-3}–10^{-4} sec is predicted. This is in general agreement with the observed lifetime,[14] which is about half that in the gas phase. Thus the low efficiency of quenching collisions, along with possible further "cage effects," does not allow the quenching to dominate the radiative decay of triplet biacetyl, and phosphorescence can be observed in the liquid.

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(11) W. E. Kaskan and A. B. F. Duncan, *J. Chem. Phys.*, **18**, 427 (1950).

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