Pressure Dependence, t-Butoxy Radical Decomposition

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The Pressure Dependence of the Rate Constant for the *t*-Butoxy Radical Decomposition Reaction

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A thermal decomposition of the *tert*-butoxy radical has been studied in the gas phase over the pressure range of 1–200 torr at 413 °K using di-*tert*-butyl peroxide + trimethylsilane mixtures. The relative rate constants were obtained by studying the competitive reactions between *tert*-butoxy radical decomposition (t-BuO· → CH_3COCH_3 + CH_3·) and hydrogen abstraction reaction from trimethylsilane (t-BuO· + $HSi(CH_3)_3$ → t-BuOH + $Si(CH_3)_3$·). The conventional RRKM calculations were carried out to compare the observed fall-off behavior of the decomposition rate constant (k_d) with the theoretical predictions using reasonable values of input parameters. In all cases the calculated half-rate pressure ($P_{1/2}$) were significantly higher than those observed. The failure of RRKM to reproduce the fall-off behavior led us to suggest that not all of vibrational modes contribute to excitation (leading to decomposition) on the same time scale.

Introduction

The pressure dependence of the rate constant of a unimolecular decomposition reaction is well known. For molecules such as cyclopropane, the "fall-off" region corresponds to pressures of a few torr. For the decomposition of free radicals, the pressure at which the rate constant becomes pressure-dependent is expected to be much higher than that for a comparably-sized molecule. This is because the activation energy, E_a, needed for the decomposition of a radical is generally appreciably less than that required for the decomposition of a stable molecule. The unimolecular reaction rate theory predicts that the pressure region at which the effect of pressure becomes apparent increases as the critical ratio, E_a/RT, decreases.

A great deal of kinetic information is now available for thermal radical decompositions, these having been studied both in pyrolysis systems and by other preparative methods such as photolysis and mercury photosensitization. The rate constants for such decompositions have been obtained by a relative method in which they are compared with those for radical–radical recombination or radical abstraction from the parent molecule. Due to the inaccuracies in the rate constants of reference reactions, large discrepancies in Arrhenius parameters have frequently been noticed.

Alkoxy radicals are known to be very important intermediate species in combustion[1], biological[2], and atmospheric chemistry[3]. The importance of these radicals has motivated numerous studies of their reactions. These studies have frequently centered on the *tert*-butoxy radicals, reflecting both the availability of thermal and photochemical sources and the advantage that the corresponding peroxide can be handled safely without any special cautions.
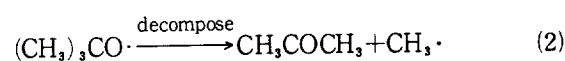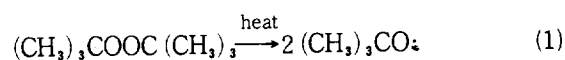
The pressure dependence for *tert*-butoxy radical decomposition was first proposed by Hershenson and Benson[4] to account for the anomalously low reported pre-exponential factors. This was demonstrated experimentally by Flowers, Batt, and Benson[5] and similar results were reported by Mulcahy and Williams[6], and Quee and Thynne[7].

Batt[8,9] studied the decomposition in the presence of nitric oxide. The system involved the use of di-*tert*-butyl peroxide as thermal sources of *tert*-butoxy radicals, and carbon tetrafluoride as an inert gas. He showed that the half-rate pressure ($P_{1/2}$) was 1 atm by studying the pressure dependence of the decomposition rate constants.

Recently, however, the contrary results have been reported by Park, Song, Lee, and Choo[10]. They obtained the absolute rate constants for *tert*-butoxy radicals with trimethylsilane and demonstrated that the rate constant of *tert*-butoxy radical decomposition did not change with addition of argon or helium as an inert third body over the pressure range of 10 torr–1 atm, indicating that $P_{1/2}$ should be much smaller than the Batt's result.

This paper presents detailed results of the pressure dependence of the rate constants of *tert*-butoxy radical decomposition to resolve above discrepancies in the fall-off behavior of the reaction. The method we have used was to decompose di-*tert*-butyl peroxide in the presence of hydrogen donor (R–H) at 140 °C. The total pressure was varied by using nitrogen, argon, methane and sulfur hexafluoride as inert gases. In the presence of hydrogen donor (R–H) the *tert*-butoxy radical reactions have two competitive pathways as shown in reaction (2) and (3).

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{\text{heat}} 2\,(CH_3)_3CO\cdot \qquad (1)$$

$$(CH_3)_3CO\cdot \xrightarrow{\text{decompose}} CH_3COCH_3 + CH_3\cdot \qquad (2)$$

$$(CH_3)_3CO\cdot \xrightarrow{\text{R–H}} (CH_3)_3COH + R\cdot \qquad (3)$$

Consequently the distribution of final products sensitively depends on the relative rate constants for reactions (2) and (3) at a given temperature. Since the rate constant of reaction (3) should show no pressure dependence, the relative ratio $[CH_3COCH_3]/[(CH_3)_3COH]$ at a given pressure will lead to the determination of the rate constant for reaction (2), from which the fall-off behavior of reaction (2) could be obtained.

A successful application of the method for the *tert*-butoxy radical reaction with trimethylsilane has been reported in this laboratory[10].

Experiments

Materials. Di-*tert*-butyl peroxide (Aldrich chemicals) was degassed and distilled several times on the vacuum line. Because of the presence of a small quantity of acetone as im-

purity, corrections were applied to the acetone produced as the result of pyrolysis. Trimethylsilane (PCR Inc.) was used without further purification.
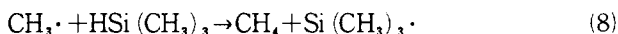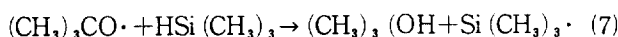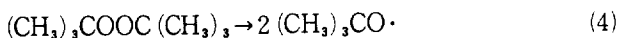
Apparatus. Experiments were carried out in a conventional static seasoned quartz reactor (volume 379 cc) which was housed in the electrically heated furnace (Lindberg)[10,12]. The feed-back temperature controller (Hana) was used to maintain the reactor temperature in ±0.5 °C. The temperature of the reactor was read by the digital temperature converter (Omega, Model 2176A) connected with chromel-alumel thermocouple (Omega, K type). The pressure measurements were done with an electronic pressure transducer (Validyne, Model CD223) and a mercury manometer. Mixture of di-*tert*-butyl peroxide vapor and trimethylsilane was made up in a reservoir (volume 6740 cc) and expanded into the reactor. The sample reservoir was wrapped with aluminium foil to protect the sample from the room light.

The reaction products were analyzed by a gas chromatograph (Yanaco, Model G-80) using a flame ionization detector (FID), which was directly connected to the reactor via a six-port sampling valve. Gas-chromatographic analysis was carried out on a Hallcomid M-18-OL column length of 2 × 2.4 m at 58 °C.

All the decomposition products were identified by comparing their retention times with those of the authentic mixture. The absolute quantities of acetone and *t*-butanol formed were measured by the calibrated standard heights of exactly known quantities of them.

Result and Discussion

When di-*tert*-butyl peroxide (DTBP) is thermally decomposed in the presence of trimethylsilane at 140 °C, the following reactions need to be considered for the fate of the *tert*-butoxy radical;

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot \qquad (4)$$

$$(CH_3)_3CO\cdot \rightarrow CH_3\cdot + CH_3COCH_3 \qquad (5)$$

$$2CH_3\cdot \rightarrow C_2H_6 \qquad (6)$$

$$(CH_3)_3CO\cdot + HSi(CH_3)_3 \rightarrow (CH_3)_3(OH + Si(CH_3)_3\cdot \qquad (7)$$

$$CH_3\cdot + HSi(CH_3)_3 \rightarrow CH_4 + Si(CH_3)_3\cdot \qquad (8)$$

$$2Si(CH_3)_3\cdot \rightarrow Si_2(CH_3)_6 \qquad (9)$$

Methyl C-H bonds in $HSi(CH_3)_3$ and DTBP are known to be much less reactive than Si-H bonds for hydrogen abstraction reactions[11].

As by-products, small peaks of C_2H_6 and $Si_2(CH_3)_6$ were detected in the GC chromatogram. No other peaks were found in our experiments.

Since we are only interested in the reactions of *t*-BuO· radical itself, reaction (6) can be excluded in our considerations. Reactions (8) and (9) are also unimportant since excess amounts of $HSi(CH_3)_3$ are always present in our reaction system.

In the case of [$HSi(CH_3)_3$] > [DTBP], we may consider only reaction (5) and (7) as the major reactions for *tert*-butoxy radicals. From equation (5) and (7) we obtain
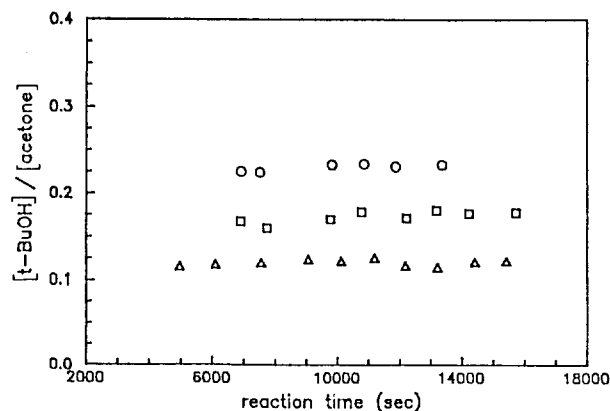
Figure 1. [*t*-BuOH]/[acetone] at various reaction times. ; Ar was used as an inert third body. △: total pressure of 43.0 torr. □: total pressure of 14.0 torr. ○: total pressure of 6.96 torr
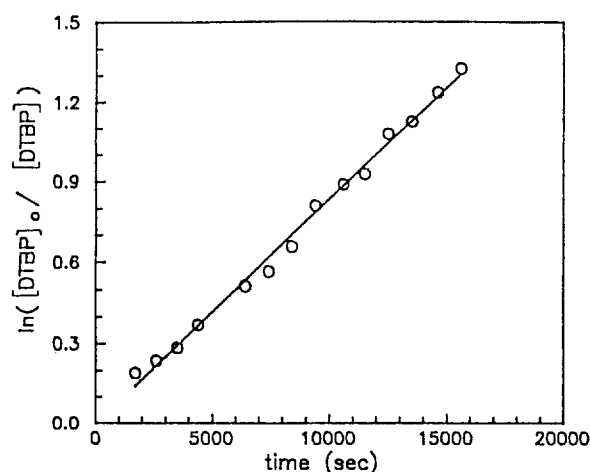

Figure 2. Plot of ln([DTBP]$_o$/[DTBP]) *vs.* time. Total pressure of 20.0 torr with added Ar gas. The slope gives k_{uni} of DTBP, 8.37 × 10^{-5} sec^{-1}.

$$\frac{[t\text{-BuOH}]}{[\text{acetone}]} = (k_a/k_d)[HSi(CH_3)_3] + C \qquad (10)$$

where C is a small and nearly constant term that is related to the fact that some *t*-BuOH was formed even though no $HSi(CH_3)_3$ was present in the system[10,12]. Under our experimental conditions, the $HSi(CH_3)_3$ concentrations were kept ca. 60 times or larger than those of DTBP in order to have the $HSi(CH_3)_3$ concentrations invariant during the experiment.

Figure 1 shows that the ratio of [*t*-BuOH]/[acetone] is independent of reaction times, which indicates the validity of our assumption that the concentration of $HSi(CH_3)_3$ is constant.

The thermal decomposition of di-*tert*-butyl peroxide (DTBP) in the gas phase has been shown to be a non-chain unimolecular process[13]. In our experiment, the concentration of DTBP decreased exponentially with time. As shown in Figure 2, a straight line was obtained when ln([DTBP]) was plotted against time. The slope gives k_{uni} of DTBP, 8.3 × 10^{-5} at 140 °C. This value reasonably agrees with the value reported by Volman *et al.*[14]

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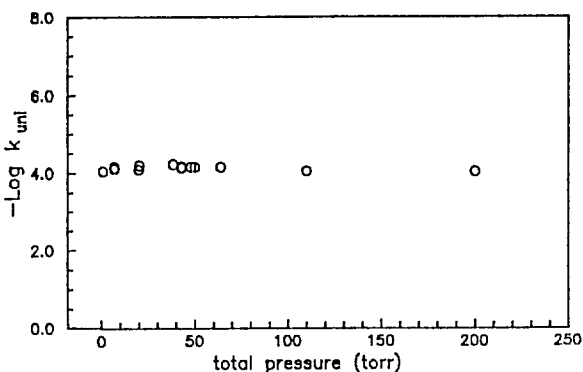
Figure 3. Pressure dependence of k_{uni} of DTBP at 140 °C. Ar was used as an inert third body.
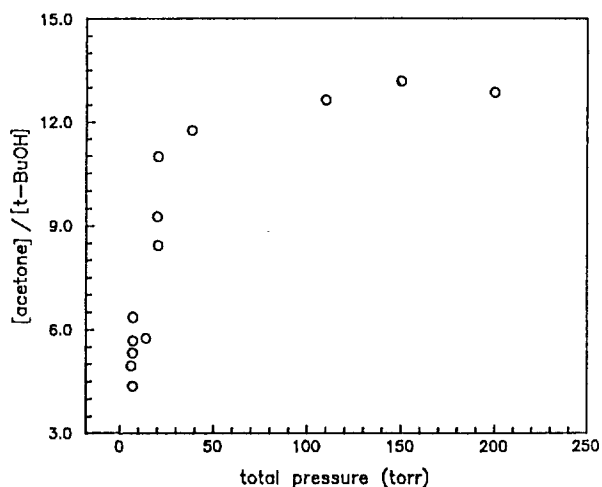
Figure 4. Pressure dependence of [acetone]/[t-BuOH] at 140 °C. Sample (DTBP + trimethylsilane) pressure: 1.00 torr. ; Ar was used as an inert third body.

Figure 3 gives plot of k_{uni} of DTBP versus total pressure. It shows that the rate constants of DTBP decomposition reaction producing *tert*-butoxy radicals are independent of total pressure when the concentration of DTBP is constant. Here, Ar was used as an inert third body to change the total pressure (1-200 torr). This result indicates that the rate constants of DTBP decomposition reactions do not change at all under our experimental conditions.

The ratios of the decomposition products, [acetone]/[t-BuOH], as a function of pressure have been calculated and plotted. A typical data is shown in Figure 4. Four different inert gases, Ar, N_2, CH_4, and SF_6 were used in order to change the total pressure. The pressure of reactants (DTBP and trimethylsilane) was kept constant at 1.00 torr for all the experiments.

By using the most reasonable Arrhenius parameters for k_a (log A = 8.5 l.mol⁻¹.sec⁻¹ and E_a = 2.1 kcal.mol⁻¹)[12], the absolute values for the decomposition rate constants were determined. The result is shown in Table 1. We also plotted log k_d versus total pressure in Figure 5.

Since the rate constant of hydrogen abstraction reaction should show no pressure dependence, from the relative ratio k_a/k_d at a given pressure, the fall-off behavior of k_d can be obtained.

Using Ar, N_2, CH_4, and SF_6 as inert buffer gases at

Table 1. The Pressure Dependence of t-BuO· Radical Decomposition Rate Constant
; Argon was used as a buffer gas.
(C = 0.082 ± 0.007)
; sample (DTBP + HSi(CH₃)₃) pressure: 1.00 torr

| Total pressure (torr)	[acetone]/[t-BuOH]	Log k
200.0	12.84	6.08
150.0	13.16	6.11
110.0	12.62	6.05
84.5	10.44	5.21
50.0	8.99	4.65
48.0	8.91	4.63
43.0	8.34	4.49
20.5	8.41	4.51
20.0	9.25	4.72
14.0	5.73	4.04
7.13	6.34	4.14
7.09	5.66	4.03
6.96	4.35	3.83
6.92	5.30	3.98
6.15	4.93	3.92
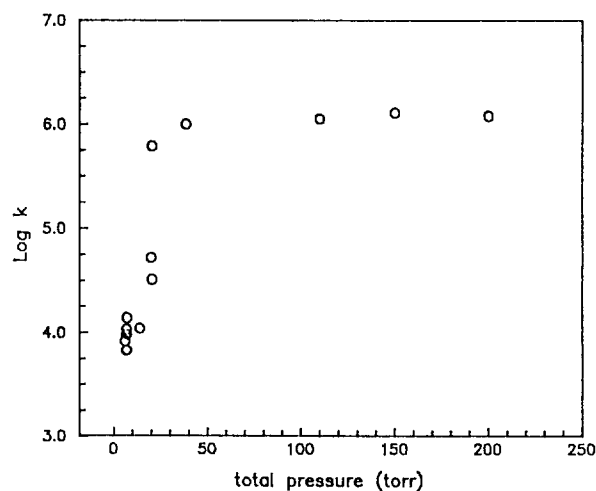
Figure 5. Pressure dependence of k_d at 140 °C. Sample (DTBP + trimethylsilane) pressure: 1.00 torr. ; Ar was used as an inert third body.

140 °C, we have obtained the "half-rate pressure" $P_{1/2}$ of 70, 50, 35, and 40 torr respectively. It was clear that Ar and N_2 were less efficient as energy transfer agents than the other two gases. In general, it is well known that energization efficiency increases with increasing molecular size qualitatively.

These values for $P_{1/2}$ are considerably smaller than those obtained by Batt and co-workers[8,9,15]. They used NO as a radical trap in a competitive study in order to obtain the absolute rate constants for the decomposition reaction:

$$t\text{-BuO·} \rightarrow CH_3COCH_3 + CH_3 · \qquad (11)$$

$$t\text{-BuO·} + NO \rightarrow t\text{-BuONO} \qquad (12)$$
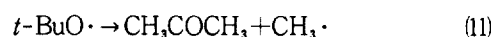
They assumed that the rate constant for reaction (12) would be pressure independent over the whole pressure

Table 2. Input Parameters for RRKM Calculations

Molecule	Activated complex
Frequencies, cm^{-1}, and degeneracies	
2980(6)	2980(6)
2900(3)	2900(3)
1465(6)	1465(6)
1350(4)	1350(4)
1220(2)	1220(2)
1106(2)	1106(1)
1013(3)	1013(2)
919(1)	919(1)
748(1)	530(2)
450(3)	450(1)
350(2)	400(2)
250(3)	350(2)
	300(2)
	260(1)
Products of moments of inertia, I_{xyz} ($\times 10^{-120}$g^{3}cm^6)	
5.60 $\times 10^6$	1.20 $\times 10^7$
L, path degeneracy	
3	1
Collision diameter	5.0 Å
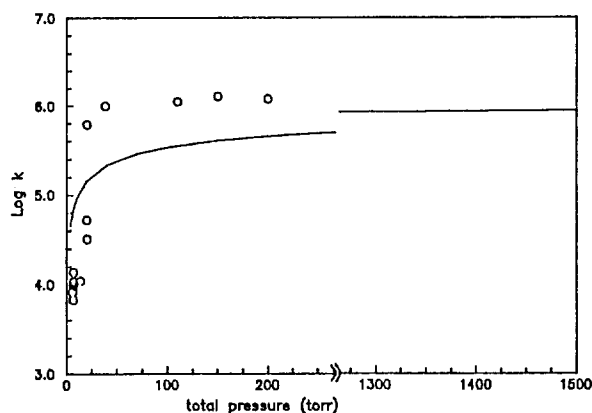
Figure 6. Plot of the observed fall-off behavior of k_d with RRKM predictions. : experimental fall-off curve (Ar was used as an inert third body). ; the solid line represents the calculated value. E_a = 15.3 Kcal/mol, log A = 14.1

range, and reported a value of 1 atm for the half-rate pressure of reaction (11). There are substantial differences in the fall-off curves obtained in the study of Batt and those which we predict from our own data. The source of this discrepancy appears to be due to the choice of reference reaction. We believe that the rate constant of the bimolecular association reaction (12) is pressure dependent. It follows that the observed pressure dependence here may be due to the pressure dependence of reaction (12) rather than reaction (11).

The conventional RRKM calculations were carried out to compare the observed pressure dependence of the decomposition rate constants with the theoretical predictions using reasonable input parameters. The vitrational frequencies used for the *tert*-butoxy radical are based upon those for *t*-butanol[16] and di-*tert*-butyl peroxide[17]. All of the input

parameters used in RRKM calculations are summarized in Table 2.

The computed fall-off curve is given with the experimental curve for comparison in Figure 6. In all cases the calculated $P_{1/2}$ were significantly higher than those observed. We found no dependence of the decomposition rate constants on pressure down to 70 torr; in sharp contrast to the fall-off curves calculated with standard RRKM codes, which indicated that for pressures below 1000 torr this system should be in bimolecular regime. These results show strong deviations from RRKM prediction.

From our experimental results, we can conclude that the failure of RRKM to reproduce the fall-off behavior is an example of non-RRKM. It may be considered that not all of vibrational modes contribute to excitation (leading to decomposition) on the same time scale[18,19].

Recently many experimental and theoretical[20] studies were published on the non-RRKM behavior. In our case the relatively low activation energy (E_a = 15.3 Kcal/mol) for the decomposition of *t*-BuO· radical could be the origin of the non-statistical energy distribution in the vibrational modes[21]. More elaborate theoretical calculation on the non-RRKM behavior is in progress.

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Association between Psoralens and Some Ionic Micelles

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Association between Psoralens and Some Ionic Micelles

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The association between psoralens and some micelles is measured by the fluorescence quenching of psoralens by methylviologen (MV^{2+}) and bromide ion in some ionic micellar solutions. The association constants were estimated to be *ca.* 10^4 for all the psoralens studied even though they show different hydrophobicity.

Introduction

Psoralens(furocoumarins), naturally occurring coumarin derivatives in various plants, have been widely used in the photochemotherapy of various skin diseases[1,2]. The photosensitivity of psoralens is primarily correlated with their photoreactivity toward pyrimidine bases in DNA under the 320–380 nm UV light[3]. Psoralens also cause damage to ribonucleic acids[4], proteins[5], and membranes[6], and are used as molecular probe for nucleic acid structure[7].

The fluorescence of psoralens in some ionic micellar solutions have been studied in our laboratory as models for biomimetic system[8]. The psoralen molecules are located in the micelle–water interfacial region and show different fluorescence features from that in aqueous solution due to both the low polarity and large viscosity of the micellar interface. The fluorescent behavior of psoralens in micellar solutions, therefore, can be used to determine their partition between the micellar and aqueous phases[9].

In general, ionic quenchers localized in the aqueous phase fail to quench the fluorescence of substrates incorporated in the micellar phase when the ion and the micellar surface are like–charged and only the substrates in aqueous phase are quenchable. The quenching data, therefore, may be used to determine the association constants between substrates and micelles[9-11].

In this paper, we would like to report the fluorescence quenching of 8–methoxypsoralen(8MOP), 5–methoxypsoralen (5MOP), 4,5′,8–trimethylpsoralen(TMP), and 5,7–dimethoxycoumarin(DMC) by ionic quenchers, Br⁻ and methylviologen(MV^{2+}) in some micellar solutions and the association constants between psoralens and micelles are calculated.

Experimental

Materials. 8MOP, 5MOP, and TMP were obtained from the Aldrich Chemical Company and used without further purification. DMC was purified by recrystallization from ethanol. Sodium dodecyl sulfate(SDS, $NaCH_3(CH_2)_{11}SO_4$, CMC = 8mM, Aldrich) was recrystallized three times from ethanol after washing with ether. Cetyltrimethylammonium bromide(CTAB, $CH_3(CH_2)_{15}N(CH_3)_3Br$, CMC = 0.94mM, Aldrich) was recrystallized twice from methanol and CTAC(cetyltrimethylammonium chloride, CMC = 1.4mM, Aldrich(25%)) was used as received. Methylviologen(1,1′-dimethyl-4,4′-bipyridinium chloride, MV^{2+}) was prepared by the method reported[12]. Sodium bromide(Junsei Chemical Co.) and sodium chloride(Kanto Chemical Co.) were used as received. Chromatographic and spectroscopic grade solvents were used for high performance liquid chromatography and emission spectroscopy, respectively. Deionized distilled water was used.

Methods. Fluorescence spectra were recorded on an Aminco–Bowman spectrofluorometer with an Amino XY recorder and/or a Perkin–Elmer LS 50 spectrofluorometer at room temperature. To compare the hydrophobicity of psoralens, high performance liquid chromatography was performed on a Waters Associates Model 244 Liquid Chromatograph equipped with Model 6000A solvent delivery system, Model 440 UV absorbance detector(254nm), and Model U6K universal injector. The Lichrosorb RP-18 column and 60% methanol eluent were used. Fluorescence quenching experiments were carried out with MV^{2+}(0-4 mM) and Br⁻(0-0.1 M) keeping the ionic strength at 0.1 by addition of sodium chloride which does not quench fluorescence. The contribution of surfactants and MV^{2+} to the ionic strength can be neglected[13].

Results and Discussion

Fluorescence Quenching. The addition of MV^{2+} and sodium bromide to the aqueous solutions of psoralens decreased the fluorescence intensity. The quenching data were analyzed by Stern–Volmer equation,