

DOUBLE-STEP VIBRATIONAL RELAXATION OF TRIPLET *p*-CHLOROTOLUENE AND *p*-DICHLOROBENZENE MOLECULES STUDIED BY THE PHOTOSENSITIZED PHOSPHORESCENCE OF BIACETYL

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Summary

The phosphorescence intensity of biacetyl photosensitized by *p*-chlorotoluene or *p*-dichlorobenzene vapour was investigated under stationary conditions in the presence of butane. The observed results indicated that the quantum yields of stable triplet formation for *p*-chlorotoluene and *p*-dichlorobenzene increased with an increase in butane pressure. Analysis of the stabilized triplet formation yield by single-step collisional deactivation of excited triplet molecules with butane led to photodecomposition rate constants for various excitation wavelengths from the 0-0 transition of sensitizers up to 271.5 nm. Double-step collisional relaxation processes by ethane and butane are postulated and discussed.

1. Introduction

A remarkable quenching effect was observed for the 253.7 nm photolysis of chlorotoluene vapour in the presence of ethane at pressures greater than 150 Torr [1], although no apparent quenching effect was observed for the photolysis of monochlorobenzene [2] and dichlorobenzene in the gas phase [3]. This sensitivity to quenching is brought about by the methyl group substitution on the monochlorobenzene ring. This result suggested that the increase in the degree of internal freedom of motion because of the methyl substituent gives rise to a longer lifetime for the excited triplet chlorotoluene molecules owing to the slow photodecomposition rate of the methyl derivatives. The small value (10^{-2}) of the fluorescence quantum yield and the collision-insensitive fluorescence lifetime (1 ns) indicated that the majority of excited singlet chlorotoluene molecules undergo intersystem crossing to excited triplet levels within a time of about 1 ns [4]. The de-

composition process therefore takes place in competition with collisional relaxation of vibrationally excited triplet molecules to stable triplet molecules in the lowest vibrational level of the $\pi^*-\pi$ triplet state.

The quantum yield for stable triplet formation was monitored for chlorotoluene and also for dichlorobenzene as a function of the pressure of a collision partner, ethane [5, 6]. In the chlorotoluene photolysis at 253.7 nm, the stable triplet formation increased gradually as the ethane pressure was increased. This indicates the collisional stabilization of vibrationally excited triplet molecules which would usually undergo dissociation [5]. The formation quantum yield of stable triplet molecules of dichlorobenzene also increased gradually as the pressure of ethane was increased [6].

The observed quantum yield of stable triplet formation, however, suggested a mechanism of stabilization of vibrationally excited triplet molecules by multiple-step collisions, except for the results for a number of excitations at longer wavelengths [5, 6], which cannot be analysed by simple Stern-Volmer kinetics. This seems to be reasonable since the amount of energy that has to be removed to stabilize the triplet molecules against C-Cl bond dissociation (dissociation energy, about 97 kcal mol⁻¹ [7]) is about 7 kcal mol⁻¹ even in the 0-0 excitation state of chlorotoluene. This value probably exceeds the average energy removed in single-step collisions with ethane [8]. The Stern-Volmer plots of the triplet formation quantum yield against the ethane pressure gave a straight line only for chlorotoluene excited at 275.5 nm (0-0 excitation). Therefore, the value of 7 kcal mol⁻¹ excess energy seems to be the upper limit for which it is valid to use Stern-Volmer kinetics assuming single-step collisions for the collisional stabilization of triplet molecules by ethane.

For dichlorobenzene, this simple Stern-Volmer mechanism of stabilization of triplet molecules by ethane via single-step collisions was found to be valid for excitations at wavelengths longer than 275.6 nm where the excess vibrational energy for C-Cl bond dissociation is less than 7 kcal mol⁻¹ [6]. For excitation wavelengths shorter than 275.6 nm ethane did not give linear plots of the inverse formation quantum yields of stable triplet molecules against the reciprocal of the ethane pressure.

Butane is believed to be a more effective vibrational energy quencher than ethane [8]. Accordingly, single-step collisional deactivation by butane is expected for excitation wavelengths slightly shorter than 275.5 nm. Indeed, when butane was used as the collision partner, the Stern-Volmer plots for the stable triplet formation quantum yield against the butane pressure gave straight lines for excitation wavelengths longer than 271.5 nm, as will be shown below.

This paper gives the results of measurements on the stable triplet formation quantum yield studied by the photosensitized phosphorescence of biacetyl with *p*-dichlorobenzene and *p*-chlorotoluene in the presence of butane. The results are compared with those obtained in the presence of ethane and are discussed in terms of the kinetics of the single- and double-step collisional deactivation of the vibrational energy.

2. Experimental details

The experimental set-up and procedure were very similar to those reported previously [5, 6] except for the use of butane as a quencher of the vibrational energy. Therefore only a brief description is given here. The light source was a combination of a xenon lamp and a monochromator (typical bandwidth, 0.2 nm full width at half-maximum (FWHM)) the intensity of which was monitored in order to correct the excitation spectrum for observation wavelengths.

The *p*-chlorotoluene sample was purified by repeated vacuum distillation and *p*-dichlorobenzene was purified by repeated recrystallization from methanol solution. Butane (stated purity, 99.9%) was available from Takachiho and was used without further purification. Biacetyl was obtained from Tokyo Kasei and distilled under vacuum. The pressures of the sample vapour and the foreign gas were measured by a capacitance manometer. The gas mixture was stirred by a glass circulator for about 1 h before each run. The measurements were carried out at room temperature. The various parameters required to estimate the triplet formation quantum yield QY_T were determined by analogy with previous work [5, 6].

3. Results and discussion

3.1. Quantum yield of triplet formation of *p*-chlorotoluene and *p*-dichlorobenzene

The excitation spectra of biacetyl phosphorescence sensitized by *p*-chlorotoluene and *p*-dichlorobenzene correspond exactly to the absorption spectra of *p*-chlorotoluene and *p*-dichlorobenzene respectively. The spectra are similar to those reported in previous papers [5, 6].

The QY_T obtained are plotted against the butane pressure in Fig. 1. The excitation wavelengths correspond to those of the vibrational peaks in the absorption spectra. The observed QY_T increases with increasing butane pressure, indicating the effect of vibrational relaxation to the stable triplet state by collisions with butane. At the highest pressure (760 Torr) of butane used in this study, QY_T for *p*-chlorotoluene reached values of about 0.8 for excitation between 275.5 and 262.4 nm, although QY_T for *p*-dichlorobenzene remains lower than that for *p*-chlorotoluene and is still increasing at 760 Torr. This suggests that there is a difference between the lifetimes of the excited triplet levels of the two molecules which is determined by the rates of non-radiative decay.

The vibrationally excited triplet molecules undergo intersystem crossing to the ground state competitively with C—Cl bond dissociation. For excitation at 253.7 nm in the presence of ethane, the sum of the quantum yield QY_d of photodissociation and that of stable triplet formation was definitely less than unity, indicating the presence of unimolecular non-radiative decay channels other than dissociation. This intersystem crossing, however, seems

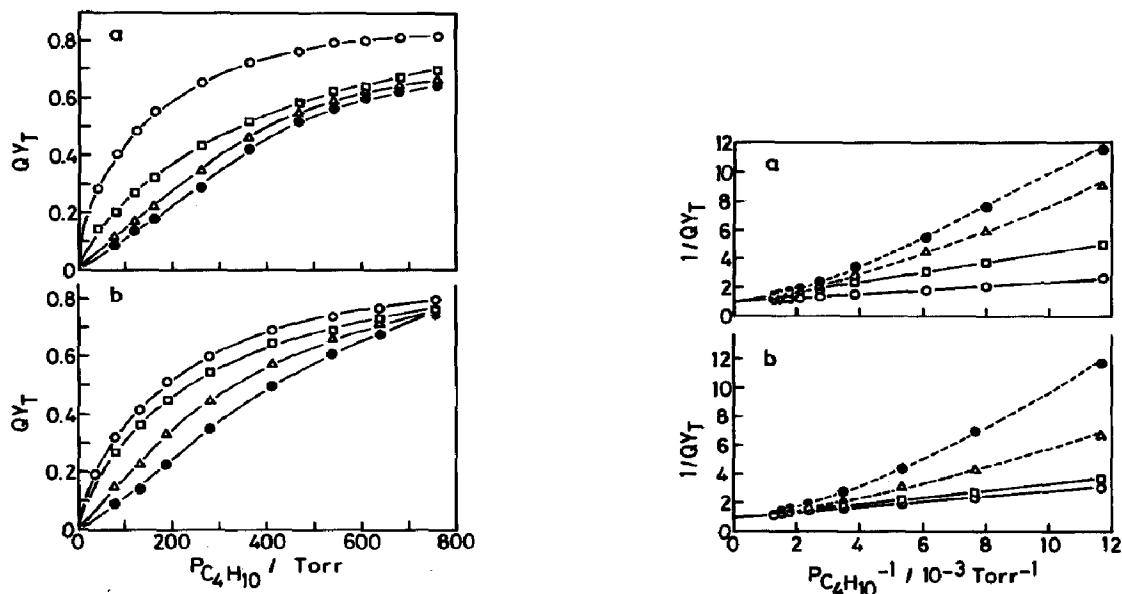


Fig. 1. Plots of quantum yields QY_T of stable triplet formation against the pressure of butane at various excitation wavelengths. (a) *p*-Dichlorobenzene (0.69 Torr) in the presence of biacetyl (0.20 Torr): \circ , 279.6 nm (0-0 transition); \square , 271.6 nm; \triangle , 266.5 nm; \bullet , 264.2 nm. (b) *p*-Chlorotoluene (1.0 Torr) in the presence of biacetyl (0.20 Torr): \circ , 275.5 nm (0-0 transition); \square , 271.5 nm; \triangle , 267.8 nm; \bullet , 262.4 nm.

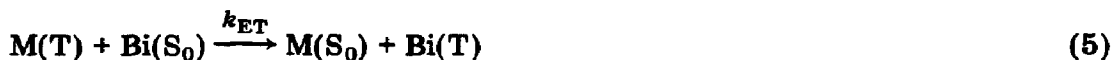
Fig. 2. Plots of the inverse of QY_T against the inverse of the butane pressure. These data were plotted from the results shown in Fig. 1. (a) *p*-Dichlorobenzene and (b) *p*-chlorotoluene. Plots for excitations at wavelengths longer than 271.6 nm for *p*-dichlorobenzene and 271.5 nm for *p*-chlorotoluene are linear; these are shown by solid lines. Broken lines show the best fit of the quadratic function given by eqn. (II) in the text.

rather slow for longer wavelength excitations in comparison with the dissociation because the QY_T tend to approach unity as the pressure of butane increases.

3.2. Single-step vibrational relaxation of triplet *p*-chlorotoluene and *p*-dichlorobenzene molecules by butane

The Stern-Volmer plots of Fig. 2 (the inverse of QY_T plotted against the inverse of the butane pressure) gave straight lines for both *p*-chlorotoluene and *p*-dichlorobenzene excited at wavelengths longer than 271.5 nm. When ethane was used as the third body instead of butane, the linear relation was obtained only for excitation wavelengths longer than 275.5 nm [5, 6]. This difference is explained by their difference in efficiency as vibrational energy quenchers.

For excitations at longer wavelengths, where linear plots are obtained between $1/QY_T$ and the inverse of the foreign gas pressure, the following reaction scheme can be derived [5, 6]:



where M, X and Bi indicate the sensitizer, the quencher and biacetyl respectively and T and S the triplet and singlet states. The QY_{T^*} are corrected for reactions (5), (6), (7) and (8) [5, 6]. The self-quenching of M(T) by the ground state sensitizer M(S₀) was shown to be negligible compared with reactions (5) and (6). Thus the relation between QY_{T^*} and the foreign gas pressure [X] can be written from the above mechanism as follows:

$$\begin{aligned} \frac{1}{QY_{T^*}} &= \frac{k_d}{k_X QY_{T^*} [X]} + \frac{1}{QY_{T^*}} \\ &= \frac{1}{QY_{T^*}} \left(\frac{k_d}{k_X [X]} + 1 \right) \end{aligned} \quad (I)$$

This equation, in conjunction with the linear plots in Fig. 2, gives the $1/QY_{T^*}$ and k_d/k_X . If a suitable value of k_X is available, we can estimate the rate k_d of the unimolecular decay of M(T^{*}). In some cases k_X may be approximated by a gas-kinetic collision frequency adjusted by an appropriate empirical factor that allows for the dependence of the efficiency on the energy transferred by collisions.

However, a large amount of energy has to be removed by collisions to bring the excited triplet molecules into stable levels before they decompose (or undergo fast intersystem crossing to S₀ levels). For *p*-chlorotoluene the excitation energy exceeds the threshold energy for C—Cl bond dissociation by about 6.7 kcal mol⁻¹ at 275.5 nm and 8 kcal mol⁻¹ at 271.5 nm. In the case of *p*-dichlorobenzene, the value ranges from 5 to 8 kcal mol⁻¹. For butane, the average vibrational energy transferred by single-step collisions is generally believed to be in the range 3 - 4 kcal mol⁻¹ [8]. For ethane as a vibrational energy quencher, the value seems to be less than for butane. Therefore, most of the highly excited triplet molecules should undergo multiple-step collisional relaxation, probably double or in some cases more, to stable triplet levels having much longer lifetimes.

After the first collisional event, the molecules distribute over the various vibrational levels. Under the present experimental conditions most molecules are populated in the levels above the threshold of C—Cl bond dissociation because the average energy removal is less than the excess excitation energy that has to be removed by collisions to stabilize the molecules to triplet levels with long lives.

If the excess excitation energy is not so large, after the first collision the molecules have energies only slightly above the dissociation limit of the C—Cl bond. The unimolecular non-radiative decay seems to be slow compared with the vibrational relaxation resulting from collisions under the present experimental conditions. Thus the molecules that experienced the first collisional event seem to be completely relaxed to stable triplet levels, giving linear plots of $1/QY_T$ against inverse pressure of butane or ethane.

Therefore, for excitation wavelengths where linear plots have been obtained for butane, values of k_d can be estimated by assuming an appropriate value of k_X ($1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$); these are listed in Table 1 for both *p*-chlorotoluene and *p*-dichlorobenzene. This value of k_X for butane is about 1.5 times larger than that for ethane ($k_X = 8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). This ratio of k_X is generally accepted as the difference in efficiency as a vibrational energy quencher between butane and ethane (for example, see ref. 9). Values of k_d thus obtained for *p*-chlorotoluene excited at 275.5 nm and for *p*-dichlorobenzene excited at 279.6, 277.2 and 275.6 nm are in reasonable agreement with the corresponding values obtained from similar linear plots for ethane [5, 6]. Although ethane does not give linear plots at excitation wavelengths shorter than 275.5 nm, the k_d listed in Table 1 are believed to be reasonable as values for relative unimolecular non-radiative decay rate constants of triplet molecules.

TABLE 1

Summary of $k_d k_X^{-1}$, k_X and k_d for *p*-chlorotoluene and *p*-dichlorobenzene in the presence of butane

<i>Molecule</i>	<i>Excitation wavelength (nm)</i>	$k_d k_X^{-1}$ ($\times 10^{-2} \text{ M}$)	k_X ($\times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$)	k_d ($\times 10^8 \text{ s}^{-1}$)
<i>p</i> -Chlorotoluene	275.5	1.0	1.3	1.3
	272.9	1.2	1.3	1.6
	271.5	1.3	1.3	1.7
<i>p</i> -Dichlorobenzene	279.6	0.8	1.3	1.0
	277.2	1.2	1.3	1.6
	275.6	1.5	1.3	2.0
	274.0	1.6	1.3	2.1
	271.6	1.9	1.3	2.5

The shortest excitation wavelengths, at which linear plots of $1/QY_T$ against the inverse $1/[X]$ of the foreign gas pressure were obtained, were similar for *p*-chlorotoluene and *p*-dichlorobenzene: 275.5 nm for *p*-chlorotoluene and 275.6 nm for *p*-dichlorobenzene with the foreign gas ethane (In the case of *o*-chlorotoluene and *m*-chlorotoluene the shortest wavelengths to give linear plots were reported to be 271.5 nm and 273.0 nm respectively [5]. However, careful re-analysis of the data indicated that the plots for low ethane pressures deviate slightly from linearity. The derived k_d are still valid since the approximation is accepted as being reasonable.); 271.5 nm for *p*-chlorotoluene and 271.6 nm for *p*-dichlorobenzene with the foreign gas butane. The threshold energies of C—Cl bond dissociation of *p*-chlorotoluene and *p*-dichlorobenzene should be similar and are estimated to be about 97 kcal mol⁻¹ [7]. The excess vibrational energies which must be removed by collisions to stabilize the triplet molecules are, therefore, not very different if the excitation wavelength is the same. The vibrational energy distribution after the first collision and the average vibrational energy removal per collision seem to be dependent on the collision partner and rather insensitive to the excited molecule in the present study. Thus, for *p*-chlorotoluene and *p*-dichlorobenzene, the threshold excitation wavelength for the linear plots is approximately determined by the vibrational energy quencher. This could also explain the experimental observation that the threshold excitation wavelength for the Stern–Volmer linear plots is independent of the k_d value, the lifetime of the vibrationally excited triplet molecules.

Values of QY_{T^*} for excitation wavelengths longer than 271.5 nm are also obtained from the intercepts of the straight lines in Fig. 2. The values obtained are close to unity within experimental error for both molecules. This result allows it to be stated confidently that optically excited *p*-chlorotoluene or *p*-dichlorobenzene molecules mostly undergo intersystem crossing to triplet levels.

3.3. Double-step vibrational relaxation by ethane

The plots of $1/QY_T$ against the inverse pressure of butane or ethane do not give a linear relation if the excitation is shifted to shorter wavelengths or if the foreign gas is reduced to very low pressures where non-radiative unimolecular decay of the triplet molecules after the first collision can compete with vibrational relaxation resulting from second collisions. Thus under these experimental conditions the plots will give the effects of the second collision.

For these experimental conditions, reactions (3) and (4) of the above mechanism (reactions (1) - (8)) must be replaced by reactions (3'), (4'), (3'') and (4''); the intermediate triplet molecules are denoted $M(T^*)$, and they undergo successive collisions:





From this modified mechanism, the relation between $1/QY_T$ and $1/[X]$ may be obtained starting with the equation

$$\frac{1}{QY_T} = \frac{1}{QY_{T^*}} \left(\frac{k_d' k_d''}{k_x' k_x'' [X]^2} + \frac{k_d'/k_x' + k_d''/k_x''}{[X]} + 1 \right) \quad (II)$$

By treating k_d'/k_x' and k_d''/k_x'' as adjustable parameters, this quadratic equation for $1/[X]$ can reproduce the non-linear plots of $1/QY_T$ versus $1/[X]$ for the ethane quencher, as shown by the broken lines in Fig. 3 (also see Table 2). The ratio k_d'/k_x' should correspond to the larger of the two adjustable parameters since the dissociation rate k_d' is expected to increase with the excitation energy.

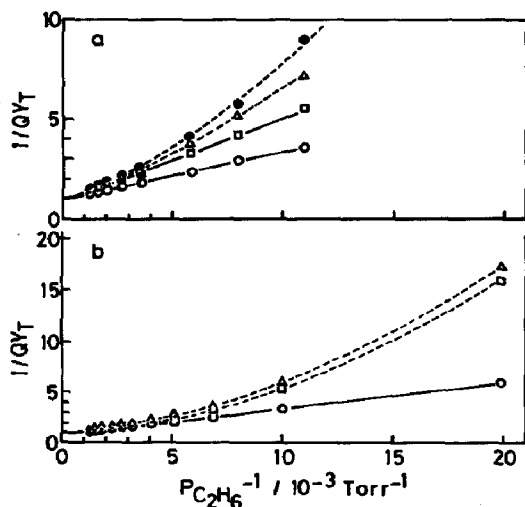


Fig. 3. Re-analysed plots of the inverse of QY_T against the inverse of the ethane pressure at various excitation wavelengths. Some of the data were taken from previous work [5, 6]. (a) *p*-Dichlorobenzene (0.57 Torr) in the presence of biacetyl (0.20 Torr): \circ , 279.6 nm (0-0 transition); \square , 275.6 nm; \triangle , 274.0 nm; \bullet , 271.6 nm. (b) *p*-Chlorotoluene (0.95 Torr) in the presence of biacetyl (0.20 Torr): \circ , 275.5 nm (0-0 transition); \square , 272.9 nm; \triangle , 271.5 nm. The plots for 275.6 nm excitation of *p*-dichlorobenzene and 275.5 nm excitation of *p*-chlorotoluene are linear, and are shown by full lines. These curved plots for shorter wavelength excitation were re-analysed by the double-step relaxation mechanism. The broken lines give the best fit to the quadratic function (eqn. (II)).

In general, precise physical meanings cannot be attributed to the values of k_d' (or k_d'') determined from these adjustable parameters (k_d'/k_x' and k_d''/k_x''). In the reaction mechanism k_x' and k_x'' were introduced to

TABLE 2

Summary of $k_d'k_X'^{-1}$, k_X' , k_d' , $k_d''k_X''^{-1}$, k_X'' and k_d'' for *p*-chlorotoluene and *p*-dichlorobenzene in the presence of ethane

Molecule	Excitation wavelength (nm)	$k_d'k_X'^{-1}$ ($\times 10^{-2}$ M)	k_X' ($\times 10^9$ M $^{-1}$ s $^{-1}$)	k_d' ($\times 10^8$ s $^{-1}$)	$k_d''k_X''^{-1}$ ($\times 10^{-2}$ M)	k_X'' ($\times 10^9$ M $^{-1}$ s $^{-1}$)	k_d'' ($\times 10^8$ s $^{-1}$)
<i>p</i> -Chlorotoluene	275.5	1.5	8.5	1.3			
	272.9	1.8	8.5	1.5	0.42	8.5	0.36
	271.5	1.9	8.5	1.6	0.42	8.5	0.35
<i>p</i> -Dichlorobenzene	279.6	1.2	8.5	1.0			
	277.2	1.9	8.5	1.6			
	275.6	2.3	8.5	2.0			
	274.0	2.4	8.5	2.1	0.24	8.5	0.20
	271.6	2.8	8.5	2.4	0.23	8.5	0.20

represent double-step stabilization only in a qualitative manner since the triplet molecules $M(T^+)$ distribute over various levels (mostly above the dissociation threshold and some below the threshold). At excitation wavelengths slightly shorter than 275.5 nm, the vibrational energy distribution of the triplet molecules $M(T^+)$ should be similar to that for 275.5 nm excitation. Therefore, k_X' may be approximated by the value of k_X used for the calculation of k_d for the excitation at longer wavelengths where linear Stern-Volmer plots are obtained. The values for *p*-chlorotoluene at 272.9 and 271.5 nm and for *p*-dichlorobenzene at 274.0 and 271.6 nm correspond reasonably to the values in Table 1 obtained from experimental results using butane as the collisional quencher of vibrations. This agreement may indicate that the double-step collisional relaxation mechanism of T^* can quantitatively explain the relation between QY_T and $[X]$. (Troe and Wieters have successively applied multistep-collisional relaxation processes to fit curved Stern-Volmer quenching plots for vibrationally highly excited toluene molecules [10]. This approach should be applicable to the results of Fig. 3. We, however, think it is reasonable to assume that two-step collisional quenching processes contribute to the rate of photodecomposition.)

Butane as a vibrational energy quencher gave non-linear Stern-Volmer plots for excitation wavelengths shorter than 271.5 nm. Values of k_d'/k_X' (and k_d''/k_X'') with butane for these excitation wavelengths were determined as adjustable parameters to give simulated plots, and hence k_d' values are also given in Table 3. The value of k_X' for butane is approximated by that of k_X (1.3×10^{10} M $^{-1}$ s $^{-1}$) for excitation at 271.5 nm. The calculated values approximately represent the relative values of the dissociation rates at various excitation wavelengths. For ethane, k_d' values at these excitation wavelengths can also be calculated, although these values are likely to be less accurate than those obtained for butane. The values are also given in Table 3.

TABLE 3

Summary of $k_d'k_X'^{-1}$, k_X' , k_d' , $k_d''k_X''^{-1}$, k_X'' and k_d'' for *p*-chlorotoluene and *p*-dichlorobenzene in the presence of ethane or butane

Quencher	Excitation wavelength (nm)	$k_d'k_X'^{-1}$ ($\times 10^{-2}$ M)	k_X' ($\times 10^9$ M $^{-1}$ s $^{-1}$)	k_d' ($\times 10^8$ s $^{-1}$)	$k_d''k_X''^{-1}$ ($\times 10^{-2}$ M)	k_X'' ($\times 10^9$ M $^{-1}$ s $^{-1}$)	k_d'' ($\times 10^8$ s $^{-1}$)
<i>p</i> -Chlorotoluene							
Ethane	270.0	2.1	8.5	1.8	0.45	8.5	0.38
	267.8	2.3	8.5	2.0	0.63	8.5	0.54
	262.4	4.0	8.5	3.4	1.2	8.5	1.0
	253.7	5.0	8.5	4.2	1.2	8.5	1.0
Butane	270.0	1.4	13	1.8	0.17	13	0.22
	267.5	1.6	13	2.1	0.36	13	0.78
	262.4	2.6	13	3.4	0.81	13	1.1
<i>p</i> -Dichlorobenzene							
Ethane	269.3	3.3	8.5	2.8	0.35	8.5	0.30
	266.5	3.6	8.5	3.1	0.53	8.5	0.45
	264.2	4.7	8.5	4.0	0.84	8.5	0.71
	253.7	9.4	8.5	8.0	4.0	8.5	3.4
Butane	269.3	2.1	13	2.7	0.19	13	0.25
	266.5	2.4	13	3.1	0.29	13	0.38
	264.2	3.0	13	3.9	0.31	13	0.40

Values of k_d'' can also be calculated from those of k_d''/k_X'' determined from the simulated plots and listed in Table 3. The increase in the dissociation rate with the excitation energy should be considered to be only qualitative.

In Fig. 2, the value of QY_{T^*} (QY_T at the limiting high pressure of butane) can be obtained by simulating the plots of $1/QY_T$ versus $1/[X]$ for butane at various excitation wavelengths. The values extrapolated to $1/[X] = 0$ are close to unity for excitation around 260 nm of both *p*-chlorotoluene and *p*-dichlorobenzene. There seems to be no apparent decrease in the formation of triplet molecules; this confirms the absence of any fast non-radiative decay channel of the photoexcited singlet molecules which is competitive with the intersystem crossing at these excitation wavelengths.

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