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PHOTOINDUCED CLEAVAGE OF CARBON-HALOGEN BOND FOR MONO-HALOGENATED 2',4',6'-TRIMETHYLBENZOPHENONES

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Yijun Tang

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PHOTOINDUCED CLEAVAGE OF CARBON-HALOGEN BOND FOR MONO-HALOGENATED 2',4',6'-TRIMETHYLBENZOPHENONES

By

Yijun Tang

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ABSTRACT

PHOTOINDUCED CLEAVAGE OF CARBON-HALOGEN BOND FOR MONO-HALOGENATED 2',4',6'-TRIMETHYLBENZOPHENONES

By

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One of the general reactions of mono-halogenated 2',4',6'-trimethylbenzophenones is the carbon-halogen bond cleavage when the reactant is exposed to ultraviolet light source with proper wavelength. This type of reaction, on which my research has been focused, is believed to be occurring from the lowest triplet states. Quenching with triplet quenchers supports such thinking as well as provides triplet lifetime of reactant molecules.

Photoinduced carbon-bromine bond cleavage and carbon-iodine bond cleavage have been studied by Professor Peter J. Wagner. By comparing with his study, some important conclusion can be made. It seems that halogenated 2',4',6'-trimethylbenzophenones have similar behavior as their non-alkyl-substituted analogues, in terms of reaction rate constant and triplet lifetime. Only apparent difference lies in the reactions of 3-bromo-benzophenones and 4-bromo benzophenones, 2',4',6'-trimethyl and non-substituted.

For iodo-2',4',6'-trimethylbenzophenones, the carbon-iodine bond cleavage is the only major pathway of deactivation of the excited triplet reactant molecules. 2-iodo-2',4',6'-trimethylbenzophenone and 4-iodo-2',4',6'-trimethylbenzophenone have a larger carbon-iodine bond cleavage constant than

3-iodo-2',4',6'-trimethylbenzophenone, which is consistent with the electron density of π^* orbital, indicating $^3(n,\pi^*)$ state is responsible for the reaction.

As for bromo-2',4',6'-trimethylbenzophenones, the quantum yields of dehalogenated 2',4',6'-trimethylbenzophenone formation from 3-bromo-2',4',6'-trimethylbenzophenone and from 4-bromo-2',4',6'-trimethylbenzophenone are very low. This may suggest some competing reactions. One likely possibility is hydrogen abstraction from solvent by the triplet ketones. 2-bromo-2',4',6'-trimethylbenzophenone undergoes more efficient carbon-bromine bond cleavage reaction with a much higher quantum yield compared to 3- and 4- bromo-2',4',6'-trimethylbenzophenones.

Both the rate constants and the quantum yields of dehalogenated ketone formation are small in the case of chloro-2',4',6'-trimethylbenzophenones because of the relatively high carbon-chlorine bond energy.

Dedicated to my parents, sister, wife and
those who made this paper possible.

For with You is the fountain of life; in Your light we see light.
Psalm 36:9

ACKNOWLEDGMENTS

First of all, I must thank Professor Peter J. Wagner. As the boss in this group and my advisor, his brilliant understanding of and invaluable experience in physical photochemistry has benefited my study so much that I never thought I would meet with any difficulties that could not be overcome in the course of my graduate life. No one got surprised when the information came that he had won the Inter-American Photochemical Society Award in Photochemistry. I also appreciate that he has guided me in selecting some critically useful courses. Professor Wagner is kind of a strict man, which comforts me in that I know I deserved whatever the title I achieved in this group. On the other hand, his sense of humor has impressed me a lot, especially when he releases those humorous remarks with a serious looking.

I would also like to thank all other professors in my committee, who are Professor James E. "Ned" Jackson, Professor Gary J. Blanchard, and Professor David P. Weliky. In the past three years, we had several enjoyable party-like committee meetings, which will be shining pearls worthy of recalling in the string of my life. I am very grateful to the precious discussion that they have offered.

I owe a lot to the following co-workers in our group: Mr. Jong-Ill Lee, Dr. Hyo-Jung Yoon, and Ms. Varsha Govardhan. The good time we have spent together in the lab bears in my mind forever.

At last but absolutely not the least, I would like to thank my loving wife Danyan for having been backing me up while we start our new life in the United States of America.

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LIST OF ABBREVIATIONS

BP ..... benzophenone
BrBP ..... bromo-benzophenone
BrM_3BP ..... bromo-2'4'6'-trimethylbenzophenone
ClBP ..... chloro-benzophenone
ClM_3BP ..... chloro-2',4',6'-trimethylbenzophenone
IBP ..... iodo-benzophenone
IM_3BP ..... iodo-2',4',6'-trimethylbenzophenone
M_3BP ..... 2',4',6'-trimethylbenzophenone
*m*BrBP 3-bromo-benzophenone
mBrM_3BP ..... 3-bromo-2'4'6'-trimethylbenzophenone
*m*ClBP 3-chloro-benzophenone
mClM_3BP ..... 3-chloro-2',4',6'-trimethylbenzophenone
*m*IBP 3-iodo-benzophenone
mIM_3BP ..... 3-iodo-2',4',6'-trimethylbenzophenone
*m*XBP 3-halo-benzophenone
mXM_3BP ..... 3-halogenated 2',4',6'-trimethylbenzophenone
*o*BrBP 2-bromo-benzophenone
oBrM_3BP ..... 2-bromo-2'4'6'-trimethylbenzophenone
*o*ClBP 2-chloro-benzophenone
oClM_3BP ..... 2-chloro-2',4',6'-trimethylbenzophenone
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*p*BrBP 4-bromo-benzophenone
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*p*IBP 4-iodo-benzophenone
pIM_3BP ..... 4-iodo-2',4',6'-trimethylbenzophenone
*p*XBP 4-halo-benzophenone
pXM_3BP ..... 4-halogenated 2',4',6'-trimethylbenzophenone
Q ..... quencher
XBP ..... halo-benzophenone
XM_3BP ..... halogenated 2',4',6'-trimethylbenzophenone

INTRODUCTION

Ketones are always the objects of study in photochemistry because the longest wavelength of absorption for the carbonyl group in ketones exceeds 280 – 300 nm.[2] Wavelength in that area can be obtained easily in most photochemistry laboratories. Carbon-halogen bond cleavage for mono-halogenated benzophenones occurs from the triplet state because of rapid intersystem crossing.[3,4] Study of the reactivity of halophenyl ketones helps us to understand the triplet state of a molecule.

A. Mechanism of carbon-halogen bond cleavage for halogenated aromatic ketones.

Carbon-halogen bond cleavage in halogenated aromatic ketones has been studied widely.[5] The mechanism has been proposed by P. J. Wagner.

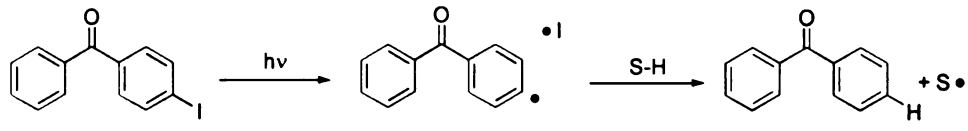


Figure 1. Mechanism of photoinduced cleavage of carbon-halogen bond for oIBP[1]

The mechanism is similar for other XBPs and XM_3BPs. Upon excitation, the carbon-halogen bond breaks and a radical pair is formed. This radical pair is believed to be an "in-cage" tight one and the two components may

diffuse apart to form free halogen atom and phenyl radical. The phenyl radical abstracts hydrogen from solvent molecule; thus, dehalogenated benzophenones are formed.

B. Competitions with carbon-halogen bond cleavage.

Mechanism of cleavage indicates a two-step reaction: bond cleavage and hydrogen abstraction. Competitions may occur at either step.

B1. Competition at bond cleavage stage: Hydrogen abstraction.

The possibility of competition from physical decay is out of the question because the research indicates that the rate of bond cleavage is on the order of 10^8 s^{-1} in cyclopentane, which is much faster than typical phosphorescence emission process.[6,7] Besides, physical radiationless decay process of ketone triplet cannot compete efficiently either.[1] Thus, I will only discuss chemical competition in this paper. In addition to bond cleavage, another decay of ketone triplet is hydrogen abstraction, intermolecular or intramolecular.

When phenyl ketone molecules abstract hydrogens from their environment instead of experiencing carbon halogen bond cleavage, α-hydroxy radicals are formed. Pinacols then are produced by coupling of such hydroxy radicals.[6] Figure 2 shows the procedure.

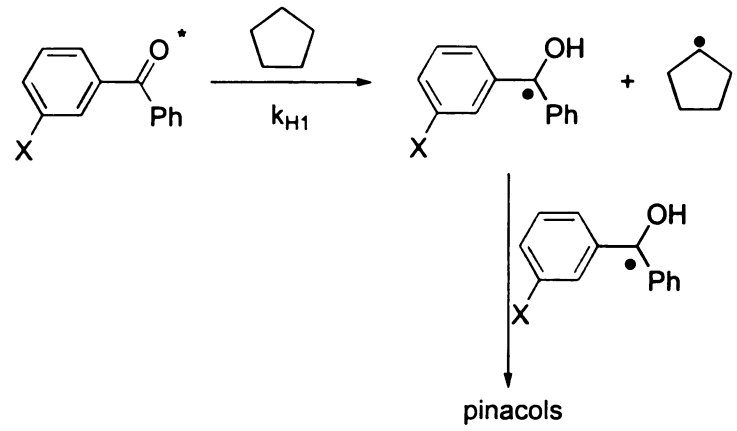


Figure 2. Fate of triplet halo-benzophenone molecules in cyclopentane. (X=Br or I)[1]

The rate of hydrogen abstraction from the environment is based on the identity of the phenyl ketones and the character of solvent molecules. When the ketone molecules contain γ-hydrogens, like benzylic hydrogen in XM_3BPs, intramolecular hydrogen abstraction may also occur. The following figure shows the process.

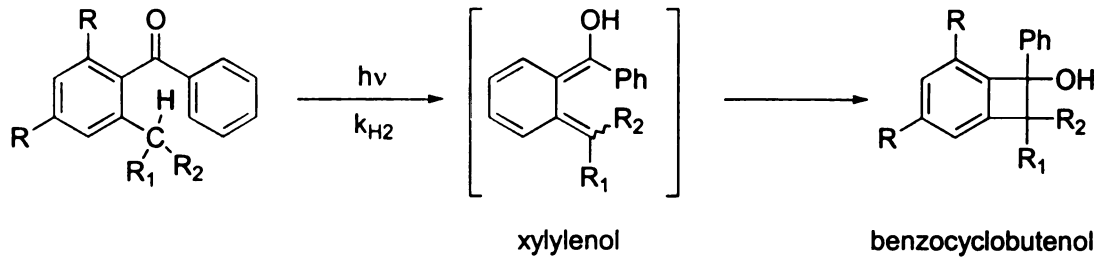


Figure 3. Benzocyclobutenol formation from 2,4,6-trialkylbenzophenones[8]

The significance of those two kinds of competition can be illustrated by the concentrations of pinacol and of benzocyclobutenol in the product mixture if there is any.

B2. Competition at hydrogen abstraction stage: Recoupling.

A contact radical pair is formed immediately after the carbon-halogen bond breaks. The fate of halogen phenyl radical pair is shown in the following figure. Again, we will just use *o*IBP as an illustration.

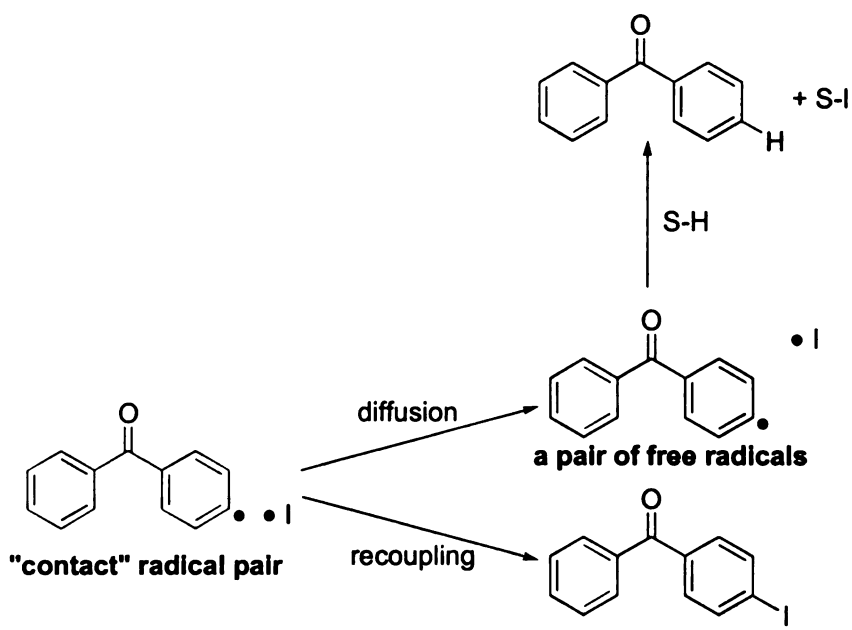


Figure 4. Fate of halogen phenyl radical pair after bond cleavage

Recoupling of halogen phenyl radical pair competes with the diffusion apart of those two radicals, which is reflected in the quantum yield of dehalogenated benzophenone formation.[1,4]

C. Electronic states of benzophenones.

As good sensitizers, benzophenone molecules induce rapid intersystem crossing between triplet states and singlet states of themselves; thus the reactivity of benzophenone is confined to the triplet states,[4] especially the lowest triplet states because of the lower energy compared to higher level triplet states. The rate of vibrational relaxation from higher triplet states to the lowest triplet states is very fast.[2,8] For this reason, I will only talk about the triplet states of benzophenone.

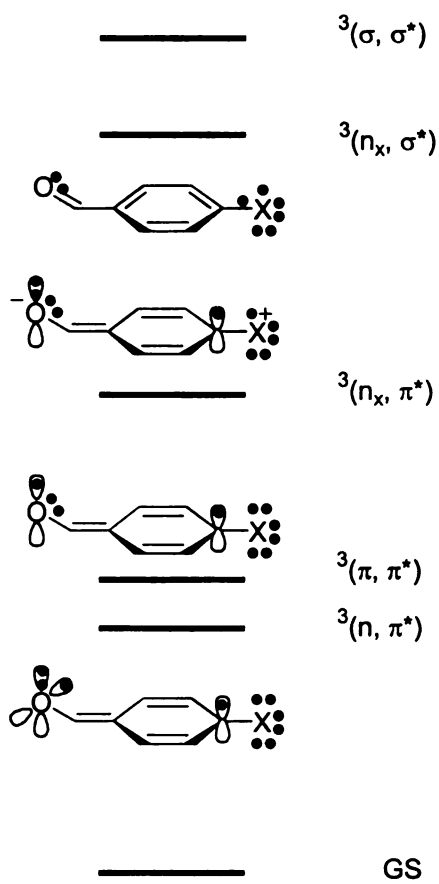


Figure 5. Energy diagram of excited triplets of halophenyl ketones[4]

The lowest triplet state of benzophenone is the $^3(n,\pi^*)$ state.[1] $^3(\pi,\pi^*)$ state is only a few kcal/mol higher than the lowest triplet state[3] and also plays an important role in the reaction.

Because of the small energy gap between $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states, both of them are considered as "reactant".[4] However, the dissociative states are $^3(\sigma,\sigma^*)$ and $^3(n_x,\sigma^*)$.[9] The coupling of "reactant" states with dissociative states is needed in the course of carbon-halogen bond cleavage.

The $^3(n,\pi^*)$ is the only state responsible for the C-X bond cleavage for iodinated benzophenones,[1,6] while the $^3(\pi,\pi^*)$ states dominates the C-X bond cleavage for brominated benzophenones.[4] The coupling of the $^3(n,\pi^*)$ state with the $^3(\sigma,\sigma^*)$ state explains the behavior of carbon-iodine bond cleavage for iodinated benzophenones.[1,6] For the isomers of brominated benzophenones, the lone pair p orbital on bromine atom couples with benzoyl π system, producing comparable coupling of "reactant" state with dissociative state.[4]

D. Kinetics and quenching study.

Figure 6 shows the pathway of the C-X bond cleavage for XM_3BPs.

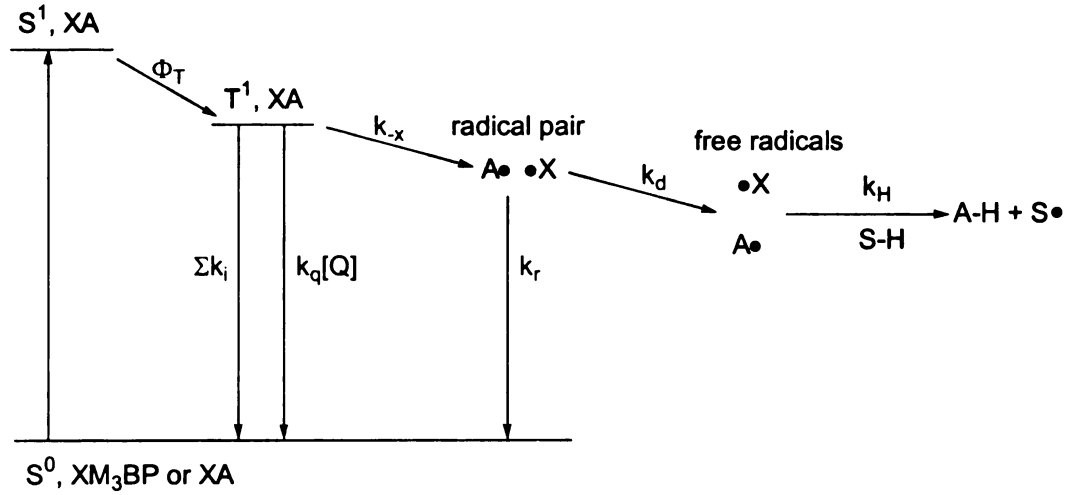


Figure 6. Mechanistic representation with rate constants

Φ_T is the quantum yield of triplet formation, which can be considered as 1 in C-X bond cleavage of benzophenones.[10] k_{-x} is the rate constant of C-X bond cleavage and k_q is the rate constant of quenching. Q is the quencher. Σk_i is the sum of the rate constants of decay pathways other than C-X bond cleavage and quenching. Actually, the only apparent competition results from intermolecular and intramolecular hydrogen abstraction (*refer to* **Part B1** of **INTRODUCTION**) based on previous studies of carbon-halogen bond cleavage from benzophenones;[1,4,6] therefore, Σk_i can be replaced with $k_{H1}[SH]$ and k_{H2}, where k_{H1} is the rate constant of intermolecular hydrogen abstraction and k_{H2} is the rate constant of intramolecular hydrogen abstraction. k_d is the rate constant of diffusion apart of the "contact" radical pair which is formed immediately after C-X bond cleavage. k_r is the rate constant of radical recoupling from

the "contact" radical pair. k_H is the rate constant of hydrogen abstraction of phenyl radicals from solvent.

The quantum yield of M_3BP formation can be expressed by the following equation.

$$\Phi = \Phi_T \cdot \frac{k_{-x}}{k_{-x} + k_q[Q] + \Sigma k_i} \cdot \frac{k_d}{k_d + k_r} \quad (1)$$

As Φ_T is almost 1[10] and Σk_i can be replaced with $k_{H1}[SH] + k_{H2}$ the above equation is revised as follows.

$$\Phi = \frac{k_{-x}}{k_{-x} + k_q[Q] + k_{H1}[SH] + k_{H2}} \cdot \frac{k_d}{k_d + k_r} \quad (2)$$

When there is no quencher added, the quantum yield is denoted as Φ_0. The following equation can be easily derived from Equation 2.

$$\Phi_0 = \frac{k_{-x}}{k_{-x} + k_{H1}[SH] + k_{H2}} \cdot \frac{k_d}{k_d + k_r} \quad (3)$$

Professor P.J. Wagner has studied the factors that affect Φ_0 and has found that it increases with increasing k_d. Viscous solvent produces smaller k_d value, which decreases Φ_0.[1,4]

From Equations 2 and 3, Stern-Volmer equation is obtained, which is shown as Equation 4.

$$\frac{\Phi_0}{\Phi} = 1 + k_q \tau [Q] \qquad (4)$$

τ is the triplet lifetime when there is no quencher. The expression of τ is shown in Equation 5.

$$\frac{1}{\tau} = k_{-x} + k_{H1}[SH] + k_{H2} \qquad (5)$$

By varying the concentration of quencher, [Q], a series of Φ_0/Φ value can be obtained. The plot of Φ_0/Φ against [Q] is a straight line with a slope of $k_q\tau$. As the value of k_q, $k_{H1}[SH]$ and k_{H2} can be obtained by reliable estimate,[10,11,14] the triplet lifetime, therefore k_{-x}, can also be obtained.

$$k_{-x} = \frac{1}{\tau} - k_{H1}[SH] - k_{H2} \qquad (6)$$

For benzophenones in cyclopentane, the value of $k_{H1}[SH]$ is less than 0.1×10^6 s^{-1} for *o*XBPs and *o*XM_3BPs; 7.6×10^6 s^{-1} for *m*XBPs and *m*XM_3BPs, and 6.3×10^6 s^{-1} for *p*XBPs and *p*XM_3BPs.[14] The value of k_{H2} is 1.7×10^6 s^{-1}.[10]

E. Goals of research.

Carbon-halogen bond cleavage of XBPs has been well studied by Professor P.J. Wagner's group; however, the same kind of cleavage of XM_3BPs has not been fully studied. The only related reports are limited to the graduation dissertation of Martin Sobczak.[8]

The purpose of my research is to understand the chemistry, in particular carbon-halogen bond cleavage of XM_3BPs. The benzene ring with three methyl groups in an XM_3BP molecule is almost perpendicular to the carbonyl group. We are interested in how that twisted benzene ring affects carbon-halogen bond cleavage. We also expect that such research might provide information that helps to understand the nature of triplet states of organic molecules.

RESULTS AND DISCUSSIONS

A. Quantum yield.

The quantum yields of M_3BP formation in cyclopentane for various XM_3BP were measured at room temperature under irradiation of 313 nm. The results are listed in Table 1.

Table 1. The quantum yields of some BPs in cyclopentane

Benzophenones	Quantum yield
***o*ClM$_3$BP**	0.0066[a]
***o*BrM$_3$BP**	0.009
***m*BrM$_3$BP**	0.0007
***p*BrM$_3$BP**	0.0013
***o*IM$_3$BP**	0.16
***m*IM$_3$BP**	0.21
***p*IM$_3$BP**	0.34
***o*BrBP**[b]	0.09
***m*BrBP**[b]	0.002
***p*BrBP**[b]	0.003
***m*IBP**[c]	0.28
***p*IBP**[c]	0.27

a. in cylclohexane
b. *ref.* **4**
c. *ref.* **1**

The quantum yield decreases in the order of *o*IM$_3$BP, *o*BrM$_3$BP, and *o*ClM$_3$BP, which is consistent with C-X bond strength. This indicates that the weaker the C-X bond is, the more readily it breaks. Former researches also indicate the similar decreasing trend of quantum yield.[1,4,5,14] The C-Cl bond does not break for ClBPs, and the quantum yield of BrBPs is smaller than that of the corresponding IBPs.

Some interesting conclusion may be made when the quantum yields of XM_3BPs are compared with those of XBPs.

For BrBPs, the *ortho* isomer has a much larger quantum yield than the *meta* or *para* isomers. The fact is also true in the case of BrM_3BPs. This has been explained by the direct through space electron transfer between bromine atom and the adjacent carbonyl group.[4,15]

B. Quenching study.

The quenching study was carried out in about 0.01M cyclopentane solution under exposure of 365 nm irradiation with naphthalene as the quencher. The reaction of acetophenone formation from 0.01M valerophenone was the actinometer. The value of $k_q\tau$ is gleaned from Stern-Volmer plot. The value of k_q for 2,4,6-trimethylbenzophenone in benzene has been measured, which is 5×10^9 $M^{-1}s^{-1}$.[11(a)] Quenching is a diffusion-controlled process; therefore, the value of k_q decreases with increasing viscosity of solvent. The value of k_q for halogenated 2',4',6'-trimethylbenzophenone in cyclopentane is estimated as 10^{10} $M^{-1}s^{-1}$ because the viscosity of cyclopentane is lower than that of benzene.[11] Stern-Volmer plots are shown in Figures 7-12 and the result of quenching study is shown in Table 3.

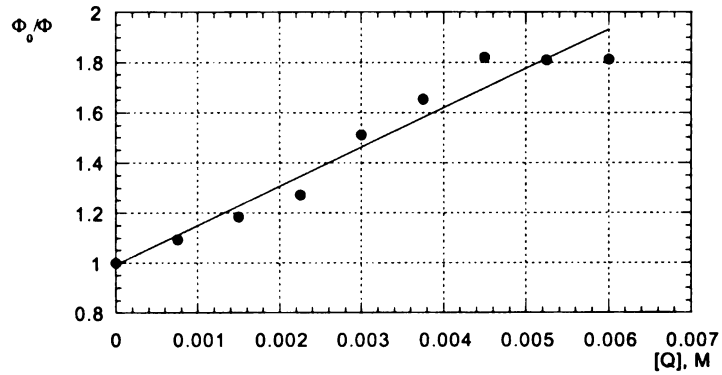


Figure 7. Quenching by naphthalene of M_3BP formation from *o*BrM_3BP

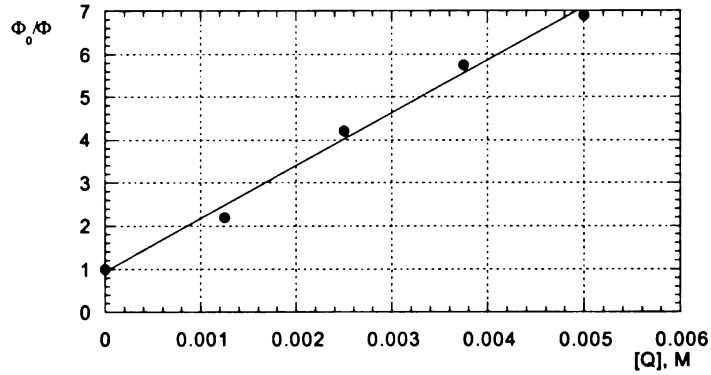


Figure 8. Quenching by naphthalene of M_3BP formation from *m*BrM_3BP

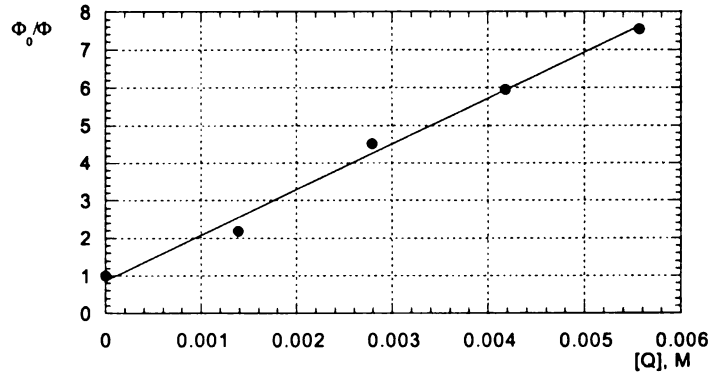


Figure 9. Quenching by naphthalene of M_3BP formation from *p*BrM_3BP

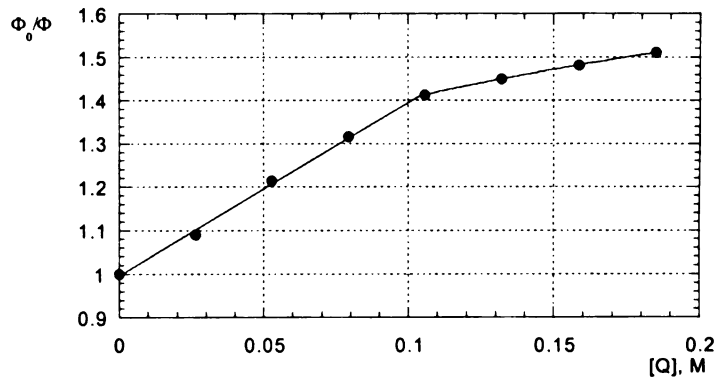


Figure 10. Quenching by naphthalene of M_3BP formation from *o*IM_3BP

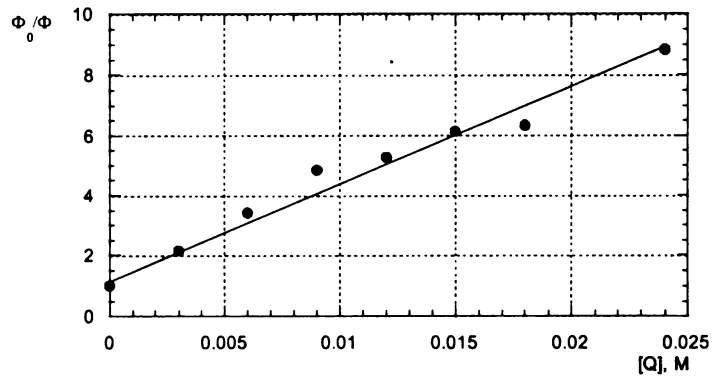


Figure 11. Quenching by naphthalene of M_3BP formation from *m*IM_3BP

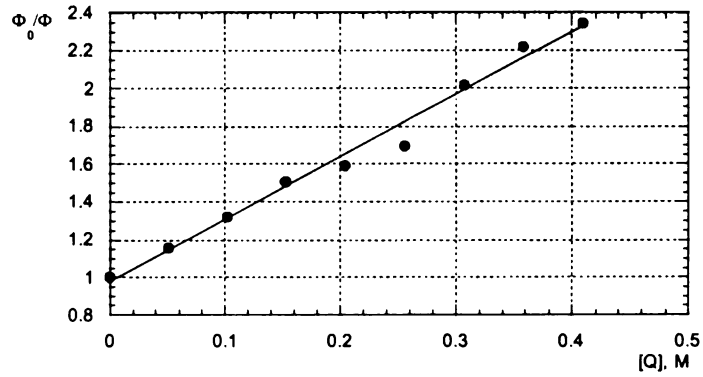


Figure 12. Quenching by naphthalene of M_3BP formation from *p*IM_3BP

Table 2. Room temperature photokinetics for some XM_3BPs in cyclopentane[a]

Benzophenones	Φ	$k_q\tau$ (M^{-1})	$1/\tau$ (10^8 s^{-1})	k_H (10^8 s^{-1}) [d]	k_{-x} (10^8 s^{-1}) [e]
***o*BrM$_3$BP**	0.009	173.5	0.58	0.017	0.56
***m*BrM$_3$BP**	0.0007	1228.7	0.081	0.093	<0.001
***p*BrM$_3$BP**	0.0013	1211.6	0.083	0.080	0.003
***o*IM$_3$BP**	0.16	3.98	25.1	0.017	25.1
***m*IM$_3$BP**	0.21	308.7	0.32	0.093	0.23
***p*IM$_3$BP**	0.34	3.31	30.2	0.080	30.1
***o*BrBP**[b]	0.09	-	0.6	<0.001	0.6
***m*BrBP**[b]	0.002	-	0.076	0.076	0.001
***p*BrBP**[b]	0.003	-	0.063	0.063	0.001
***m*IBP**[c]	0.28	265	0.37	0.076	0.30
***p*IBP**[c]	0.27	3.0	32	0.063	32

a. $k_q = 10^{10}$ $M^{-1}S^{-1}$ (*ref.* **11**);

b. *ref.* **4**;

c. *ref.* **1**;

d. for XBPs, $k_H=k_{H1}[SH]$; for XM_3BPs, $k_H=k_{H1}[SH]+k_{H2}$; $k_{H1}[SH]$ is assumed to be $<0.001\times10^8$ s^{-1}, 0.076×10^8 s^{-1}, and 0.063×10^8 s^{-1} for *o*X(M_3)BPs, *m*X(M_3)BPs and *p*X(M_3)BPs in that order (*ref.* **14**); $k_{H2} = 0.017\times10^8$ s^{-1} (*ref.* **10**);

e. k_{-x} is obtained according to Equation 6.

The photochemistry of XM_3BPs is almost the same as that of XBPs. *Meta* brominated isomers have comparable C-X bond cleavage rate constants as *para* brominated isomers, while *meta* iodinated isomers C-X bond cleavage rate constants almost 100 times faster than *para* iodinated isomers.

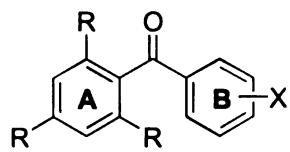
This phenomenon has been thoroughly explained by P.J. Wagner.[1,4,6] Only the $^3(n,\pi^*)$ state is responsible for the cleavage reaction for iodinated benzophenones,[1,6] while $^3(\pi,\pi^*)$ state dominates the dissociation process for brominated benzophenones.[4] A major difference between those two kinds of triplet states is that both *meta* and *para* electron-donating

substituents interact very strongly with the benzoyl π system in the $^3(\pi,\pi^*)$ states.[16] Consequently, the strong interaction gives comparable coupling with dissociative states; thus carbon halogen bond cleavage rate constants for *meta* and *para* brominated benzophenones are almost the same. On the contrary, halogen atoms do not interact equally at *meta* and *para* positions for iodinated benzophenones since the "reactant" state for iodinated benzophenones is $^3(n,\pi^*)$. The spin density in the π^* orbital is much larger at *para* position than at *meta* position,[17] which is thought to be the reason that iodinated benzophenones shows great positional dependency.[1]

For IBPs and IM_3BPs, the triplet decay rate constant is almost the same as the C-I bond cleavage rate constant since C-I bond cleavage is the only apparent decay process. However, hydrogen abstraction from solvent competes with C-Br bond cleavage for BrBPs (*refer to* **Part B1** of **INTRODUCTION**). The hydrogen abstraction rate is on the order of 10^7 s^{-1} for BrBPs in cyclopentane,[4,6,8] which is much faster than the rate constant of C-Br bond cleavage. Therefore, further investigation is needed to find out the rate constant of hydrogen abstraction for $XBrM_3BPs$, in order that the carbon halogen bond cleavage rate constant can be figured out.

C. Conclusion

We have found that XM_3BPs bear similar photophysical and photochemical characters as XBPs although the molecular geometries are different.



X= Cl, Br, or I
R= H or CH_3

Benzene ring **A** is almost conjugated with the carbonyl group for XBPs while it is perpendicular to the carbonyl group for XM_3BPs.[8] It indicates that carbon-halogen bond cleavage on benzene ring **B** is not significantly affected when the geometry of benzene ring **A** changes from a coplanar ring to a perpendicular ring. In another word, the twisted ring **A** does not change carbon halogen bond cleavage a lot.

EXPERIMENTAL

A. Synthesis.

Generally speaking, XM_3BPs were made according to the following scheme.

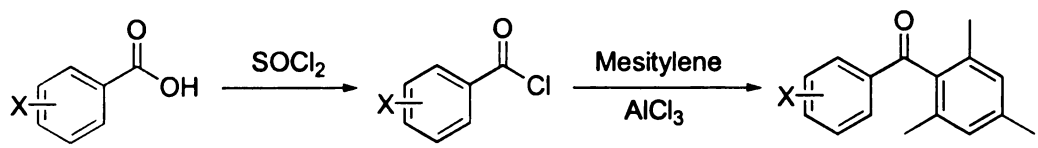


Figure 13. Synthesis of XM_3BP

The intermediate chlorides might be solids or oil substances. The final products are all solids.

As the photochemical study does not require much amount of chemicals, I concentrated on purity of the product more than on the yield. In most occasions, several times of recrystallization were needed.

A1. Chloro-2',4',6'-trimethylbenzophenones.

3.75g appropriate chlorobenzoic acid was refluxed with 30 mL thionyl chloride for about 12 hours. At this point, the reactant mixture was a clear solution. The excessive thionyl chloride was removed and crude acid chloride was obtained. The crude acid chloride was dissolved in a small amount of 1,2-dichloroethane.

A mixture of 3.8g aluminum chloride, 3.5g mesitylene and 25 mL 1,2-dichloroethane was cooled to 0°C. The acid chloride was then added into the mixture drop by drop. The reaction mixture was stirred for 24 hours. Then the reaction was quenched with a mixture of 15mL concentrated hydrochloric acid and 60g ice. The aqueous layer was extracted with dichloromethane twice. The combined organic layer was washed with water, 5M sodium hydroxide and water, twice each, and then was dried over magnesium sulfate. The solvent was removed and the crude product was recrystallized from petroleum ether. Charcoal might be needed if the color of product is not white.

oClM$_3$BP:

^{1}H-NMR (benzene-d_6, 300MHz, δ ppm): 2.06 (s, 3H), 2.07 (s, 6H), 6.62 (s, 2H), 6.69 (m, 2H), 7.07 (dd, 5.7, 1.2 Hz, 1H), 7.38 (dd, 7.2, 1.8 Hz, 1H);

^{13}C-NMR ($CDCl_3$, 75MHz, δ ppm): 19.7, 21.1, 126.8, 128.8, 131.5, 131.7, 132.7;

FTIR (KBr, cm^{-1}): 761(s), 916(s), 1252(s), 1437(s), 1586(s), 1674(vs), 2363(w), 2916(br);

GC-MS (m/z): 147.1(52.79%), 208.0(57.94%), 223.0(100%), 257.1($M^{+\cdot}$), 259.2($M^{+\cdot}$).

***p*ClM$_3$BP:**

^{1}H-NMR ($CDCl_3$, 300MHz, δ ppm): 2.07 (s, 6H), 2.33 (s, 3H), 6.90 (s, 2H), 7.41 (d, 8.7 Hz, 2H), 7.74 (d, 8.7 Hz, 2H);

^{13}C-NMR ($CDCl_3$, 75MHz, δ ppm): 19.3, 21.1, 128.4, 129.1, 130.7, 134.1;

FTIR (KBr, cm^{-1}): 812(s), 903(s), 1091(s), 1167(s), 1274(s), 1572(s), 1655(s), 1925(m), 2907(br);

GC-MS (m/z): 147.0(100%), 208.2(47.92%), 223.2(97.62%), 257.1($M^{+\cdot}$), 259.2($M^{+\cdot}$).

A2. Bromo-2',4',6'-trimethylbenzophenones.

5g appropriate bromobenzoic acid was refluxed with 8 mL thionyl chloride and 25 mL chloroform for about 4 hours. At this point, the reactant mixture was a clear solution. The solvent and unreacted thionyl chloride were removed and crude acid chloride was obtained. The crude acid chloride was dissolved in a small amount of 1,2-dichloroethane.

A mixture of 4g aluminum chloride, 3.6g mesitylene and 25 mL 1,2-dichloroethane was cooled to 0°C. The acid chloride was then added into the mixture drop by drop. The reaction mixture was stirred for 24 hours before the reaction was quenched by a mixture of 15mL concentrated hydrochloric acid and 60g ice. The aqueous layer was extracted with dichloromethane twice. The combined organic layer was washed with water, 5M sodium hydroxide and water, twice each, and then was dried over magnesium sulfate. The solvent was removed and the crude product

was recrystallized from ethanol. Charcoal might be needed if the color of product is not white.

***o*BrM$_3$BP:**

^{1}H-NMR (benzene-d_6, 300MHz, δ ppm): 2.01 (s, 3H), 2.07 (s, 6H), 6.61 (s, 2H), 6.67 (m, 2H), 7.30 (d, 2.4 Hz, 1H), 7.33 (dd, 7.8, 1.5 Hz, 1H);

^{13}C-NMR ($CDCl_3$, 75MHz, δ ppm): 19.8, 21.1, 127.3, 128.8, 131.8, 132.7, 134.9, 135.3;

FTIR (KBr, cm^{-1}): 897(s), 1242(s), 1292(s), 1433(s), 1584(s), 1674(s);

GC-MS (m/z): 147.1(80.60%), 208.1(97.01%), 223.2(100%), 302.2($M^{+\cdot}$), 304.2($M^{+\cdot}$).

***m*BrM$_3$BP:**

^{1}H-NMR (benzene-d_6, 300MHz, δ ppm): 1.94 (s, 6H), 2.07 (s, 3H), 6.60 (m, 3H), 7.20 (m, 1H), 7.56 (d, 7.8 Hz, 1H), 8.21 (t, 1.8 Hz, 1H);

^{13}C-NMR ($CDCl_3$, 75MHz, δ ppm): 19.3, 21.1, 128.0, 128.4, 130.3, 131.9, 134.1, 136.3;

FTIR (KBr, cm^{-1}): 1260(s), 1420(s), 1560(s), 673(s);

GC-MS (m/z): 147.0(100%), 208.2(45.65%), 223.2(79.57%), 302.2($M^{+\cdot}$), 304.2($M^{+\cdot}$).

***p*BrM$_3$BP:**

^{1}H-NMR ($CDCl_3$, 300MHz, δ ppm): 2.04 (s, 6H), 2.31 (s, 3H), 6.87 (s, 2H), 7.56 (d, 9.0 Hz, 2H), 7.64 (d, 8.7 Hz, 2H);

^{13}C-NMR ($CDCl_3$, 75MHz, δ ppm): 19.2, 21.1, 128.4, 130.8, 132.1, 134.0, 136.0, 136.1, 138.8;

FTIR (KBr, cm^{-1}): 834(s), 892(s), 1051(s), 1158(s), 1265(s), 1440(s), 1585(s), 1658(s), 1931(w), 2917(br);

GC-MS (m/z): 147.0(81.36%), 208.0(67.80%), 223.1(100%), 302.1($M^{+\cdot}$), 304.1($M^{+\cdot}$).

A3. Iodo-2',4',6'-trimethylbenzophenones.

5g appropriate iodobenzoic acid was refluxed with 8 mL thionyl chloride and 25 mL chloroform for about 4 hours. At this point, the reactant mixture was a clear solution. The solvent and unreacted thionyl chloride were removed and crude acid chloride was obtained. The crude acid chloride was dissolved in a small amount of 1,2-dichloroethane.

A mixture of 3.2g aluminum chloride, 2.9g mesitylene and 25 mL 1,2-dichloroethane was cooled to 0°C. The acid chloride was then added into the mixture drop by drop. The reaction mixture was stirred for 24 hours before the reaction was quenched by a mixture of 15mL concentrated hydrochloric acid and 60g ice. The aqueous layer was extracted with dichloromethane twice. The combined organic layer was washed with water, 5M sodium hydroxide and water, twice each, and then was dried

over magnesium sulfate. The solvent was removed and the crude product was recrystallized from petroleum ether. Charcoal might be needed if the color of product is not white.

oIM_3BP:

^{1}H-NMR ($CDCl_3$, 300MHz, δ ppm): 2.09 (s, 6H), 2.29 (s, 3H), 6.85 (s, 2H), 7.13 (m, 1H), 7.31 (m, 2H), 8.04 (d, 7.2 Hz, 1H);

^{13}C-NMR ($CDCl_3$, 75MHz, δ ppm): 19.7, 21.1, 128.0, 128.7, 131.6, 132.7, 135.2, 142.0;

FTIR (KBr, cm^{-1}): 889(s), 1003(s), 1275(s), 1415(s), 1607(s), 1666(s);

GC-MS (m/z): 147.0(54.60%), 208.0(80.46%), 223.0(100%), 350.0($M^{+\cdot}$).

***m*IM_3BP:**

^{1}H-NMR ($CDCl_3$, 300MHz, δ ppm): 2.05 (s, 6H), 2.31 (s, 3H), 6.88 (s, 2H), 7.15 (t, 7.8 Hz, 1H), 7.66 (d, 7.8 Hz, 1H), 7.88 (d, 7.8 Hz, 1H), 8.16 (t, 1.8 Hz, 1H);

^{13}C-NMR ($CDCl_3$, 75MHz, δ ppm): 19.4, 21.1, 94.8, 128.4, 128.7, 130.5, 134.2, 137.8, 138.8, 139.0, 142.2;

FTIR (KBr, cm^{-1}): 847(s), 1169(s), 1261(s), 1419(s), 1555(s), 1607(s), 1666(s), 2335(w);

GC-MS (m/z): 147.0(100%), 208.0(56.34%), 223.0(88.73%), 350.1($M^{+\cdot}$).

***p*IM$_3$BP:**

^{1}H-NMR ($CDCl_3$, 300MHz, δ ppm): 2.04 (s, 6H), 2.30 (s, 3H), 6.87 (s, 2H), 7.48 (d, 8.4 Hz, 2H), 7.79 (d, 8.4 Hz, 2H);

^{13}C-NMR ($CDCl_3$, 75MHz, δ ppm): 19.5, 21.3, 102.5, 128.6, 130.9, 134.3, 136.7, 138.3, 138.9

FTIR (KBr, cm^{-1}): 818(s), 977(s), 1141(s), 1259(s), 1437(s), 1553(s), 1666(s), 1922(m), 2952(br);

GC-MS (m/z): 147.0(59.84%), 208.0(65.35%), 223.0(100%), 350

Table 3. Melting points of XM$_3$BPs

Benzophenones	M.P. (°C)	M.P. *lit.* (°C)
***o*ClM$_3$BP**	101.0~101.5	99~101.8 [18]
***p*ClM$_3$BP**	68.0~68.5	67~69.5 [19]
***o*BrM$_3$BP**	110.9~111.0	113~115 [20]
***m*BrM$_3$BP**	84.5~85.5	86~87 [21]
***p*BrM$_3$BP**	70.5~71.2	70~73 [22]
***o*IM$_3$BP**	94.5~95.0	97~98 [23]
***m*IM$_3$BP**	84.0~84.5	85~86 [23]
***p*IM$_3$BP**	78.0~79.0	72~73 [23]

UV and phosphorescence

XM$_3$BPs have shown similar UV and phosphorescence spectroscopic characters as corresponding XBPs.

Table 4. Spectroscopic features of some benzophenones [a]

Benzophenones	λ_{max} (nm)	n, π^* λ_{max} (nm)	Phosphorescence 0, 0 in nm (kcal/mol)
*o*ClM$_3$BP	214.8	335	-
*o*BrM$_3$BP	214.4	338	-
*o*IM$_3$BP	220.2	342	-
*m*IM$_3$BP	226.2	341.9	441 (64.9)
*p*IM$_3$BP	206.0	341.2	437 (65.5)
*o*BrBP[b]	-	-	412 (69.5)
*m*IBP[c]	-	347	419 (68.3)
*p*IBP[c]	-	348	422 (67.8)

a. The sample concentration is about 0.01M in cyclopentane for UV spectra and about 0.0001M in 1:1 MeOH/EtOH for phosphorescence.
b. *ref.* **4**
c. *ref.* **1**

B. Identification.

Varian 3400 gas chromatograph and Hewlett-Packard 3392A integrator were used. Product from C-X cleavage was identified by comparing its retention time with the retention time of authentic M_3BP. The column was DB-210 50% tri-fluoropropyl methyl polysiloxane. The temperature of column was programmed as: 3 minutes at 80°C, increasing to 200 at the rate of 10°C/min., and then staying at 200°C infinitely. The temperature of the injector was 200°C and that of the detector was 220°C. The pressure of carrier gas helium was set at 80 lbs per square inch. The injection amount was 2 μL.

The coincidence of retention time indicated the C-X cleavage product was dehalogenated 2,4,6-trimethyl benzophenone.

C. Quantum yields.

Quantum yields depict efficiency of certain process such as formation of some product and some decay pathways of excited states. In my

research, I studied the quantum yield of dehalogenated benzophenone formation. The quantum yield is defined as the following equation.

$$\Phi = \frac{[P]}{I_a} \tag{7}$$

where [P] is the concentration the product formed and I_a is the intensity of light absorbed by reactant molecules.

[P] was measured by gas chromatography with hexadecane as the internal standard. I_a was measured by an chemical actinometer. In chemical actinometry, a photochemical reaction with well-known and wide-accepted quantum yield is used to quantify the intensity of absorbed light by reactant molecules.[2] In my research, I used the reaction of acetophenone formation from valerophenone.

$$\Phi_{known} = \frac{[acetophenone]}{I_a} \tag{8}$$

where Φ_{known} is the well-known and wide-accepted quantum yield under experimental conditions, [acetophenone] is the concentration of acetophenone formed from valerophenone and I_a is the intensity of light absorbed by valerophenone molecules.

The following instruments were used: 1) Rayonet photochemical reactor; 2) Photo chem lamp UV 450W immer type produced by Ace Glass

Incorporated; and 3) Shimadzu UV-160 UV-visible recording spectrophotometer with Hewlett-Packard 3393A integrator. The XM_3BP sample and valerophenone were exposed to the same light source for the same time at room temperature. The UV spectra had indicated that almost all photons were absorbed by either valerophenone molecules or XM_3BP molecules; therefore, the I_a in Equation 7 is the same as the I_a in Equation 8. The quantum yield can be calculated according to Equation 9, which is derived from Equations 7 and 8.

$$\Phi = \frac{[P]}{[acetophenone]} \cdot \Phi_{known} \qquad (9)$$

D. Quenching study.

Naphthalene was used as the quencher. To accomplish quenching study, ten culture tubes were charged with 2.8 mL about 0.01 M XM_3BP solution. Each culture tube also contained internal standard, whose concentration was the same and could be calculated out exactly. The first culture tube was free of quencher and the other nine culture tubes were loaded with quencher of different concentration. The quencher concentration in those tubes were all known.

The ten culture tubes were degassed by three circles of freeze-vacuum-thaw. Then, the ten culture tubes were set on a merry-go-round apparatus and were exposed to UV light.

After some time of irradiation, the concentration of product M_3BP was detected by gas chromatography. Under the experimental condition, the $[P]_0/[P]$ value is the same as the Φ_0/Φ value in Equation 4.

$$\frac{\Phi_0}{\Phi} = 1 + k_q \tau [Q] \qquad (4)$$

$[P]_0$ is the concentration of formed M_3BP when quencher was absent and [P] is the concentration when quencher was in presence. The value of $k_q\tau$ was obtained from the Stern-Volmer plot of Φ_0/Φ against [Q].

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