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Kinetic Studies of the Photoreaction of Benzophenone with Furan[1)]

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The photoreaction of benzophenone with furan was studied kinetically in a benzene solution. A reaction mechanism was proposed, and the rate constants of elementary reactions were determined. Benzophenone gives primarily oxetane with furan through the $n-\pi^*$ lowest triplet state. Benzophenone reacts with the oxetane initially formed to afford a 2 : 1-adduct or to decompose that to the starting materials. The ratio of the addition to the decomposition is 1 : 4. The simplest scheme for the direct cycloaddition of a benzophenone triplet and an alternate scheme involving a biradical intermediate are discussed; the second scheme is more acceptable. The rate of the formation of the intermediate is considerably slower in a benzophenone-furan system than in a benzophenone-ketenimine system (*ca.* 1/10). The formation of oxetane is greatly dependent on the ratio of the bond-forming to the bond-breaking of the biradical intermediates, which are efficiently formed (4.2×10^7 M^{-1} sec^{-1} for furan and 4.0×10^7 M^{-1} sec^{-1} for oxetane).

A number of experiments on the photochemistry of carbonyl compounds have been carried out. The hydrogen abstraction reactions were investigated in detail by flash photolysis,[2)] kinetic studies,[3)] and so on.[4)] The reaction mechanisms and the rate constants were determined. While the formation of oxetanes was first established by Paterno[5)] and various oxetanes have recently been synthesised, by the photoaddition of various carbonyl compounds to olefins, the formation conditions and the mechanisms have been discussed only from a synthetic point of view.[6)] Until recently little attention has been paid to a quantitative study of the cycloaddition. In our previous papers, we reported the synthesis of oxetanes by the reactions of carbonyl compounds with furan.[7)] In the present work, in order to determine the mechanism and the rate constants of these reactions, we investigated kinetically the reaction of benzophenone with furan; the results will be compared with the case of ketenimine.[8)]

Experimental

Materials. Benzene was treated with concentrated sulfuric acid, washed with water, and finally purified by distillation over sodium. Benzophenone was recrystallized several times from ethanol; mp 48.0—48.5°C. Naphthalene was sublimed twice; mp 79—80°C. Furan was obtained as has been described previously.[7)] Oxetane was prepared by the photoreaction of benzophenone with furan, purified by recrystallization from ethanol; mp 103—104°C. Benzhydrol was recrystallized from petroleum ether; mp 65—66°C.

Apparatus and Procedure. The light source was a 400 W high-pressure mercury lamp. The light was filtered through a Toshiba UV-DIV filter, which transmitted 7, 41, and 51% of the 3130, 3340, and 3660 Å mercury lines respectively. About ninety percent of the passed light was 3660 Å. The lamp was placed at the focal point (15 cm) of a quartz lens in order to produce a parallel beam of light across the sample. Quartz spectrophotomeric cells ($1\times1\times4.5$ cm) were extended with a graded seal and attached to a vacuum line. Each sample was degassed below 10^{-3} mmHg with alternate cycles of freezing and thawing by means of an oil diffusion pump, and then sealed off. Experiments were performed at room temperature (10—20°C), because the quantum yields of the reaction were independent of the temperature (5 and 30°C) within the range of experimental error. During the irradiation the voltage was maintained at 100V with a stabilizer (Nippon Denki-kizai Co., Model EMA-101). The light intensities were in the range of $(2—2.5)\times10^{17}$ quanta/min·cm^2. The intensity was determined with the potassium ferrioxalate actinometer described by Parker.[9)] This actinometer was used with a quantum yield of 1.18.

1) Organic Photochemical Reactions. VI. Part V. S. Toki and H. Sakurai, *Tetrahedron Letters*, **1967**, No. 42, in printed. Presented at the 19th and 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966 and March, 1967.

2) a) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961). b) J. A. Bell and H. Linschitz, *J. Am. Chem. Soc.*, **85**, 528 (1963).

3) W. M. Moore, G. S. Hammond and R. P. Foss, *ibid.*, **83**, 2789 (1961) and following papers.

4) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

5) E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, **39**, 341 (1909).

6) D. A. Arnold, R. L. Hinman and A. H. Glick, *Tetrahedron Letters*, **1964**, 1425; N. C. Yang, M. Nussim, M. J. Jorgenson and S. Murov, *ibid.*, **1964**, 3657; N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964).

7) S. Toki, K. Shima and H. Sakurai, This Bulletin, **38**, 760 (1965); K. Shima and H. Sakurai, *ibid.*, **39**, 1806 (1966).

8) L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 598 (1967).

9) C. A. Parker, *Proc. Roy. Soc. (London)*, **A220**, 104 (1953).

Kinetic Studies of Benzophenone with Furan. Samples of benzophenone and furan with or without naphthalene in benzene were degassed and irradiated. The optical densities at 345 mμ were periodically measured by means of a Hitachi EPU-2A spectrophotometer, and the residual benzophenone was determined.

Kinetic Studies of Benzophenone with Oxetane. Benzene solutions of benzophenone (0.006 M) and oxetane (0.02 M) were placed in ultraviolet cells with a breakable seal, degassed, sealed off, and irradiated with a 366 mμ light. The benzophenone was determined by the absorption at 345 mμ; after the irradiation, furan and the solvent were collected by trap-to-trap distillations. The furan was determined, by means of gas chromatography (Dinonyl phthalate, 3 m, 80°C, Hydrogen flame detector), from the ratio of the peak areas to the cyclohexane added as an internal standard.

Identification of Furan. The trap-to-trap distillate contained a compound with a peak at a position similar to that of furan in gas chromatography, and the Carr-Price test was positive. When the distillate was treated with maleic anhydride, 2, 5-endoxa-1, 2, 5, 6-tetrahydrophthalic anhydride was isolated.

Results and Discussion

Kinetic Studies of Benzophenone with Furan. In the photoreaction of benzophenone with furan, oxetane (6, 6-diphenyl-2, 7-dioxa-(3, 2, 0)-hept-3-ene) was prepared; no by-product was obtained except for the further product of the oxetane produced initially in the prolonged irradiation. When benzophenone alone was irradiated in benzene, the spectral change was very little; an iso-absorptive point was fortunately observed at 345 mμ, which is the λ-maximum of benzophenone. At this point the absorption of oxetane is negligible ($\varepsilon_{\text{oxetane}} < 1$, $\varepsilon_{\text{benzophenone}}$ 127). The reduced bepzophenone, therefore, can be determined from the absorption at 345 mμ, which may be considered to be equal to the formation of oxetane. This assumption is reasonable, because the quantum yield of the reduction of benzophenone and the life-time of benzophenone triplet are in good agreement with the observations of Hammond and his co-workers.[3]

The reaction rate is simply proportional to the absorption of light under our conditions. In this case the rate formula for a run can be derived as follows:

$$-\mathrm{d}C/\mathrm{d}t = (\Phi I_0/d)(1 - e^{-\alpha c d}) \times 1000,$$

where I_0 is the intensity of the incident light; α, the average molar absorbancy, 165[10]; Φ, the quantum yield of the formation of oxetane; d, the length of the reaction vessel; and c, the concentration of benzophenone.

Integration gives:

$$\ln(e^{\alpha c d} - 1) = -1000\,\alpha\Phi I_0 t + \ln(e^{\alpha c_0 d} - 1).$$

Hence, the plot of $\ln(e^{\alpha c d} - 1)$ against t should give a straight line with a slope of $1000\alpha\Phi I_0$. The quantum yield, therefore, can be obtained from the slope.

The plots of $\ln(e^{\alpha c d} - 1)$ *vs.* t are shown in Fig. 1. As will be discussed later, there was an accompanying benzophenone-photosensitized decomposition of oxetane, so the plots deviate from the straight lines. Although this tendency appeared greatly in the run of the low concentration of furan on account of the higher conversion, the slope at the time zero leads to the quantum yield of the formation of oxetane at the initial stage.

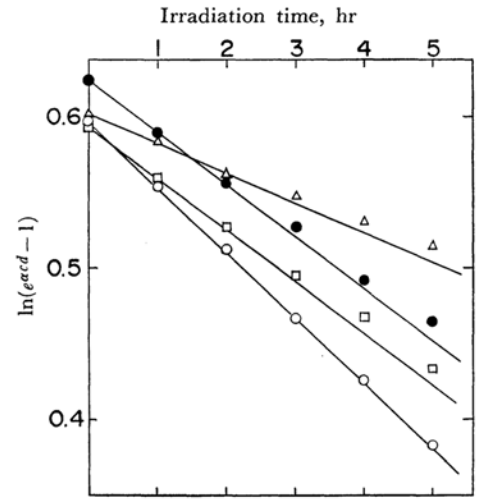


Fig. 1. Fading curves of benzophenone for various concentration of furan.
Benzophenone 0.006 M
Furan △ 0.0041 M □ 0.0088 M
● 0.0157 M ○ 0.0714 M

It has been reported that, in hydrogen-atom abstraction and in the formation of oxetane, the reaction proceeds *via* the n-π^* triplet state of carbonyl compounds.[6] By analogy with this, the reaction species is the triplet state of benzophenone, because the reaction was quenched by oxygen or naphthalene, which are very effective quenchers of the triplet state, and because the long-lived benzophenone triplet was involved. The simplest possible scheme (Scheme 1), therefore, is as follows:

Scheme 1

$$\mathrm{B} \xrightarrow{h\nu} \mathrm{B}^s \text{ (excited singlet state)} \quad (0)$$

$$\mathrm{B}^s \xrightarrow{k_1} \mathrm{B} \quad (1)$$

$$\mathrm{B}^s \xrightarrow{k_2} \mathrm{B}^t \text{ (lowest triplet state)} \quad (2)$$

$$\mathrm{B}^t \xrightarrow{k_3} \mathrm{B} \quad (3)$$

$$\mathrm{B}^t + \mathrm{F} \xrightarrow{k_4} \mathrm{B} + \mathrm{F} \quad (4)$$

$$\mathrm{B}^t + \mathrm{F} \xrightarrow{k_5} \mathrm{Ox} \quad (5)$$

10) The value is on the average of five determinations.

$$B^t + B \xrightarrow{k_6} 2B \quad (6)$$

$$B^t + Q \xrightarrow{k_7} B + Q^t \quad (7)$$

where B, F and Q represent benzophenone, furan, and the quencher respectively. The kinetic analysis of Scheme 1 leads to the following rate law:

$$1/\Phi_{ox} = ((k_1 + k_2)/k_2)(1 + k_4/k_5 + (k_3 + k_6[B] + k_7[Q])/k_5[F]) \quad (I)$$

The plot of $1/\Phi_{ox}$ against $1/[F]$ at a constant concentration of benzophenone without naphthalene gives a straight line with a slope of 0.26 M, and with an intercept of 35 that indicates a limiting quantum yield of 0.0286 (Fig. 2). By taking $k_1 \ll k_2$,[3] k_4/k_5 is 34 from the intercept. In order to determine the absolute rate constants, the quantum yield was measured in a series of experiments in which the ketone and furan concentrations were kept constant, while the naphthalene concentration was varied. The plot of the reciprocal of the quantum yield against the naphthalene concentration is shown in Fig. 3.

Assuming that process (7) is diffusion-controlled ($k^7 = 2\times10^9$ M^{-1} sec^{-1} [11]), the slope of the line gives k_5 1.2×10^6 M^{-1} sec^{-1}. Thus, k_4 is 4.1×10^7 M^{-1} sec^{-1}.

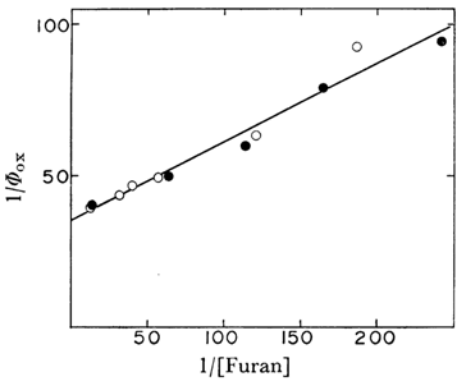


Fig. 2. Effect of furan concentration on quantum yield of formation of oxetane.
● Benzophenone 0.006 M
○ 0.012 M

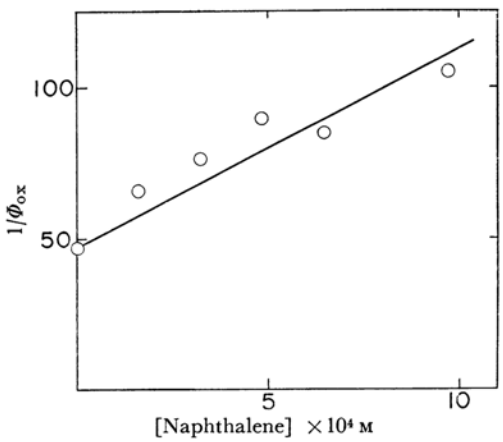


Fig. 3. Naphthalene quenching for quantum yield of formation of oxetane.
Benzophenone 0.012 M
Furan 0.0249 M

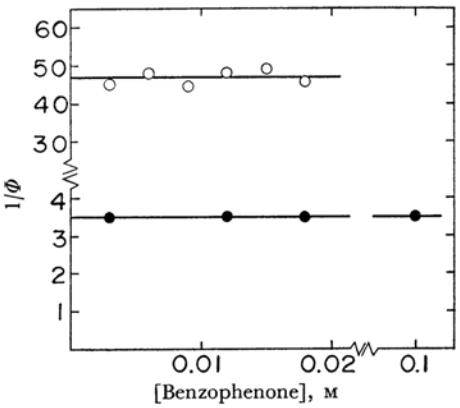


Fig. 4. Reciprocal of quantum yields of formations of oxetane and benzpinacol in regard to benzophenone concentration.
○ Oxetane in benzophenone-furan
● Benzpinacol in benzophenone-benzhydrol
(Furan 0.0203 M; Benzhydrol 0.10 M)

Figure 4 gives the plots of the reciprocal of the quantum yields of the formation of oxetane and benzpinacol *versus* the concentration of benzophenone. The fact that the quantum yields of the cycloaddition and the photoreduction reactions are independent of the concentration of the ketone (0.002—0.10 M) indicates that k_6 (the self-quenching of benzophenone) is negligible. The slope of the line in Fig. 2 shows that the value of k_3/k_5 is 0.26. Thus k_3[12] is 3.1×10^5 sec^{-1}. This gives a value of 3.2×10^{-6} sec for the average life time for the triplet state. This value is in good agreement with the data of Hammond *et al.*[3] (3.8×10^{-6} sec) and Bäckström *et al.*[4] (1.9×10^{-6} sec).

Let us now examine the observed values of k_4 and k_5. The triplet energy of benzophenone is lower than that of furan, because in the reverse order the formation of oxetane would not occur,[13] because the triplet-triplet energy transfer from molecules with lower triplet levels to those with

11) G. Porter and F. Wilkinson, *Proc. Roy. Soc. (London)*, **A264**, 1 (1961).

12) k_3 may involve the second order deactivation process;

$$B^t + \bigcirc\!\!\!\!\bigcirc \rightarrow \left[BH\cdot + \bigcirc\!\!\!\!\bigcirc^{\cdot}\right] \rightarrow B + \bigcirc\!\!\!\!\bigcirc$$

(see Ref. 2b).

13) The formation of oxetane from the reaction of olefin triplet with benzophenone in ground state (J. Saltiel, R. M. Coates and W. G. Dauben, *J. Am. Chem. Soc.*, **88**, 2745 (1966).) could be negligible, if any, under our condition of the low concentration of benzophenone (0.006 M).

higher triplet levels is very slow, 10^3—10^4 $M^{-1}\cdot sec^{-1}$.[14] The addition reactions at sufficiently low activation energies are considerably faster than the hydrogen abstraction reaction. The observed rate constant for the cycloaddition of benzophenone to furan, k_5, is comparable to that for the abstraction reaction from benzhydrol, and considerably smaller than that for the addition to ketenimines $(4—5)\times 10^8$ $M^{-1}sec^{-1}$.[8] In view of the above facts, it can be considered that k_4 is too large and k_5, too small.

A second scheme, Scheme 2, seems to be more satisfactory; it involves an intermediate, (B—F)*:

Scheme 2

$$B \xrightarrow{h\nu} B^s \quad (0)$$

$$B^s \xrightarrow{k_1} B \quad (1)$$

$$B^s \xrightarrow{k_2} B^t \quad (2)$$

$$B^t \xrightarrow{k_3} B \quad (3)$$

$$B^t + F \xrightarrow{k_4} B + F \quad (4)$$

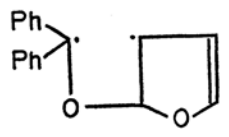
$$B^t + F \xrightarrow{k_8} (B\text{-}F)^* \quad (8)$$

$$(B\text{-}F)^* \xrightarrow{k_9} Ox \quad (9)$$

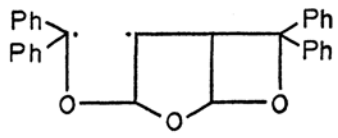
$$(B\text{-}F)^* \xrightarrow{k_{10}} B + F \quad (10)$$

$$B^t + Q \xrightarrow{k_7} B + Q^t \quad (7)$$

In this scheme the benzophenone triplet is quenched by furan directly and indirectly. The intermediate is probably a biradical structure, I, for the preferential structure is a more stable biradical intermediate,[7] and the more stable the intermediate, the less the quantum yield. Similar biradical intermediates have been proposed in the isomerization of olefins by carbonyl compounds.[15]



I



II

The rate law drawn from this scheme is given in Eq. (II):

$$1/\Phi_{ox} = ((k_1 + k_2)/k_2)((k_9 + k_{10})/k_9) \times (1 + k_4/k_8 + (k_3 + k_7[Q]/k_8[F]) \quad (II)$$

From the intercept in Fig. 2, $0<k_{10}/k_9\leqq 35$. Considering the ratio of bond-forming to bond-breaking for II ($k_{13}/k_{12}=20$) (which will be described later), $20\leqq k_{10}/k_9\leqq 35$. Structure I, having an allyl radical, is more stable than structure II, so the biradical I is more apt to decompose into benzophenone and furan. Supposing that the ratio of k_{10} to k_9 is the maximum value, 35, the intercept and the slope in Fig. 2 and the slope in Fig. 3 give a negligible k_4 value and a k_8 value of 4.2×10^7 $M^{-1}sec^{-1}$. These values are reasonable considering the results in ketenimines.

In this reaction, the rate of the formation of I is quite slow, and the ratio of the bond-forming to the bond-breaking of I (k_9/k_{10}) is very small in comparison with the case of a benzophenone-ketenimines system. These facts may be qualitatively interpreted as reflecting the difference in electron density between furan and ketenimine and the stability between I and a benzophenone-ketenimine complex.

Kinetic Studies of Benzophenone with Oxetane, A solution of benzophenone (0.006 M) and oxetane (0.02 M) in benzene was irradiated with a 366 mμ light. Furan formed and the amount of benzophenone increased, as is shown in Fig. 5.

Scheme 3, which also involves biradical intermediates, is expressed as follows:

Scheme 3

$$B^t \xrightarrow{k_3} B \quad (3)$$

$$B^t + Q \xrightarrow{k_7} B + Q^t \quad (7)$$

$$B^t + Ox \xrightarrow{k_{11}} (B\text{-}Ox)^* \quad (11)\ 0.72$$

$$(B\text{-}Ox)^* \xrightarrow{k_{12}} 2:1\text{-Adduct} \quad (12)\ 0.035$$

$$(B\text{-}Ox)^* \xrightarrow{k_{13}} B + (B\text{-}F)^{**} \quad (13)\ 0.68$$

$$(B\text{-}F)^{**} \xrightarrow{k_{14}} Ox \quad (14)\ 0.54$$

$$(B\text{-}F)^{**} \xrightarrow{k_{15}} B + F \quad (15)\ 0.14$$

$$B^t + F \xrightarrow{k_{16}} Ox \quad (16)$$

The formation of the 2 : 1-adduct[16] reduces

14) W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., "Advances in Photochemistry," Vol. III, Interscience Publishers, New York, N. Y. (1964), p. 258; W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

15) J. J. Bohning and K. Weiss, *ibid.*, **88**, 2893 (1966).

16) Although it is reported (M. Ogata, H. Watanabe and H. Kanō, *Tetrahedron Letters*, **1967**, 533) that two 2 : 1-adducts are obtained, we could not detect except for an only product (symmetrical adduct); 51% yield based on the oxethane used. If an unsymmetrical adduct forms, it is a small amount, so that no attention is paid to this study, since it may not affect on kinetics. Moreover, a mechanism is proposed which involves addition of I to benzophenone in its ground state, but it is ruled out on the basis of the quantum yield of the reduced benzophenone (see Fig. 4).

benzophenone, while the decomposition[17] equivalently increases benzophenone and furan. In addition to these reactions, benzophenone adds to furan in the mechanism described above, which is simply shown in Eq. (16); thus, both benzophenone and furan decrease. As Fig. 5 shows, the rates of the formation of benzophenone and furan reduce with the irradiation time because of the secondary reaction. The slopes at the time zero in Fig. 5, however, give the ratio of the formation of the 2 : 1-adduct to the decomposition, 1: 4, in the first stage.

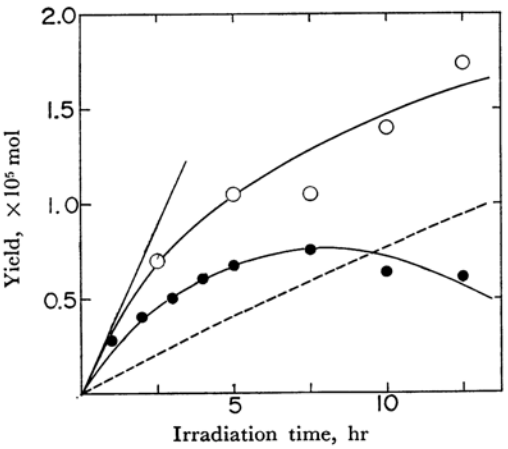


Fig. 5. Yields of formed furan and increased benzophenone in benzophenone-oxetane system.
○ Formed furan (A)
● Increased benzophenone (B)
---- A-B
(Benzophenone 0.006 M, Oxetane 0.02 M)

The kinetic analysis of Scheme 3 in the first stage leads to the following rate law:

$$\frac{1}{\Phi_{\Delta B}} = \frac{(k_{12}+k_{14})(k_{14}+k_{15})}{k_{13}k_{15}-k_{12}(k_{14}+k_{15})} \times\left(1+\frac{k_3}{k_{11}[\mathrm{Ox}]}+\frac{k_7[\mathrm{Q}]}{k_{11}[\mathrm{Ox}]}\right) \qquad \text{(III)}$$

where $\Phi_{\Delta B}$ is the quantum yield of the increased benzophenone. In order to determine the absolute rate constants, the quantum yield of the increased benzophenone was measured as the function of the added naphthalene. As is shown in Fig. 6,

17) The mechanism of the sensitized decomposition will be reported in the following paper.

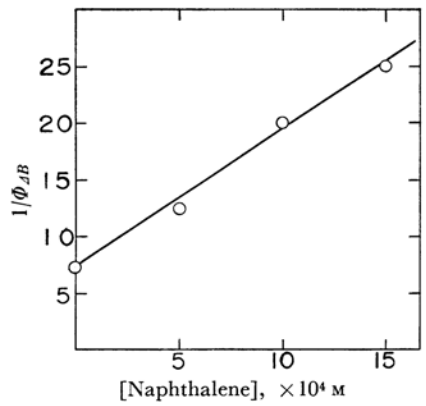


Fig. 6. Naphthalene quenching for quantum yield of increased benzophenone.
Benzophenone 0.006 M
Oxetane 0.02 M

the kinetic plot of $\Phi_{\Delta B}$ *vs.* the concentration of naphthalene gives a good linear relationship. From the ratio of the addition to the decomposition:

$$k_{12}(k_{14}+k_{15})/k_{13}k_{15} = 1/4 \qquad \text{(IV)}$$

The substitution of $k_{13}k_{15}$ from Eq. (IV) into Eq. (III) gives:

$$1/\Phi_{\Delta B} = ((k_{12}+k_{13})/3k_{12}) \times (1 + k_3/k_{11}[\mathrm{Ox}] + k_7[\mathrm{Q}]/k_{11}[\mathrm{Ox}]) \qquad \text{(V)}$$

From the intercept and the slope of Fig. 6 using k_3 of 3.1×10^5 sec^{-1} leads to a k_{11} value of 4.0×10^7 M^{-1} sec^{-1}. By using k_{11} we can evalute the quantum yields of the elementary reactions, which are written on the right side in Scheme 3. The ratio of bond-forming to bond-breaking is 1 : 20 for (B-Ox)* and 3.7 : 1 for (B-F)**, as determined from the quantum yields of the elementary reactions, while the ratio for (B-F)* in the benzophenone-furan system is 35. These differences among the biradicals can be qualitatively elucidated by means of the vibrational energy. The vibrational energies of the biradicals increase in the following order:

$$\text{(B-F)}^{**} \ll \text{(B-Ox)}^{*} \ll \text{(B-F)}^{*}$$

The decomposition is preferred to the radical coupling with an increase in the vibrational energy. On the other hand, in the case of ketenimine, the ratio of coupling to the decomposition of the complex is 4 : 10.