

PHOTOCYCLOBUTENOLIZATION OF 2,4,6-TRIISOPROPYLBENZOPHENONE AND ITS DERIVATIVES STUDIED BY PICO- AND NANOSECOND SPECTROSCOPY

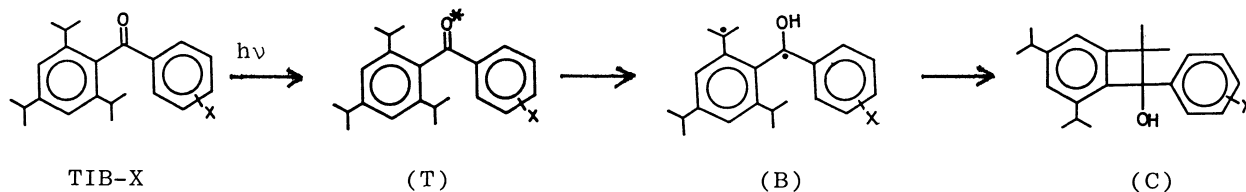
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By pico- and nanosecond spectroscopy methods, the transient absorption spectra and lifetimes of the triplet states of 2,4,6-triisopropylbenzophenones, the 1,4-biradicals and the dienols were measured. The decays of the $T^1 \leftarrow T_1$ absorptions were accompanied by the rate matching increase in the absorptions of the biradicals.

The photochemical conversions of 2,4,6-triisopropylbenzophenones (TIB-X) into the corresponding benzocyclobutenols (C) have been studied extensively,¹⁻⁶⁾ and the primary process of the reaction is thought to be the triplet ketone (T) formation followed by the 1,4-biradical (B) formation via intramolecular hydrogen-abstraction:



To obtain a more detailed knowledge of the reaction mechanisms, we have carried out the pico- and nanosecond laser photolyses of TIB-X in benzene at room temperature. The abbreviated forms of X are listed in Table 1.

The second harmonics (347.2 nm) from a picosecond mode-locked⁷⁾ and a nanosecond Q-switched⁸⁾ ruby lasers were used for sample excitation and time resolutions were 30 ps and 20 ns, respectively. For the picosecond laser photolysis, the sample solutions in a cell of 2-mm path length were not deaerated, while those for the nanosecond photolysis were deaerated in a cell of 10-mm path length. The sample concentrations were adjusted to make the absorbance to be nearly unity at 347.2 nm.

Figure 1 shows the transient absorptions of 2,4,6-triisopropylbenzophenone (TIB-H) in benzene, observed by pico- and nanosecond laser photolyses

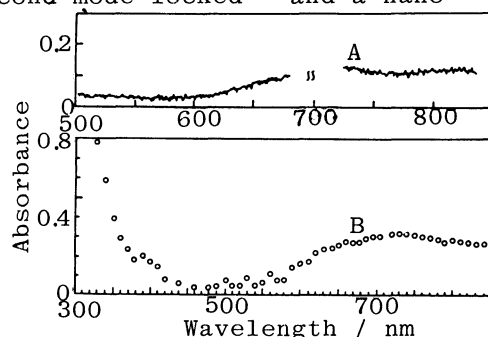


Fig. 1. Transient absorption spectra of TIB-H at 100 ps (A) and 100 ns (B).

at delay times of 100 ps (A) and 100 ns (B), respectively. In Spectrum A, the absorption around 700 nm could not be observed on account of the strong intensity of the fundamental light of 694.3 nm. However, Spectra A and B are essentially the same and they can be assigned to the $T' \leftarrow T_1$ absorption of TIB-H, based on the following facts; (1) the lifetime of Spectrum B at 77 K in EPA was equal to that of phosphorescence, i.e., ≈ 0.2 ms, (2) Spectrum B is identical to the $T' \leftarrow T_1$ absorption of TIB-H observed by Hayashi et al.²⁾

Similar spectra were also obtained for TIB-X with $X=4'\text{-CH}_3$, $4'\text{-Bu}^t$, $4'\text{-CN}$, $4'\text{-OCH}_3$, and $3'\text{-CO-Ph}$. Since the $T' \leftarrow T_1$ absorptions of benzophenone⁹⁾ and 2-methylbenzophenone¹⁰⁾ have the characteristic bands at ≈ 530 nm, the geometrical molecular structure of TIB-X may be modified by the interaction of the carbonyl group with two bulky isopropyl groups at 2- and 6-positions. This may give rise to the appearance of the $T' \leftarrow T_1$ absorption bands at ≈ 700 nm instead of those at ≈ 530 nm.

The time-evolution of the $T' \leftarrow T_1$ absorption of TIB-H was determined by measuring the absorbance (ΔOD) at 670 nm as shown in Fig. 2. The experimental points (closed circles) give the average $\Delta OD(t)/\Delta OD(\infty)$ of all shots at each delay time, and the error bars give the deviation from the average. $\Delta OD(\infty)$ was determined by averaging data at 2 ns. (For the sake of comparison, the result for 2-methylbenzophenone is shown by the open circles,¹⁰⁾ where the absorbance was measured at 520 nm.) It is evident that band growth reaches a plateau after about 60 ps and its intensity remains constant up to 2 ns. The full curve corresponds to the instrumental response function calculated by a well-known convolution method,¹¹⁾ by assuming 30 ps gaussian probe and excitation pulse shapes. Since this pulse width was determined by measuring the buildup of $T' \leftarrow T_1$ absorption of benzophenone in n-heptane and the rate of intersystem crossing of benzophenone is very rapid, i.e., 8 ps,¹¹⁾ it can safely be concluded that the rate of intersystem crossing is also rapid in TIB-H. The rapid buildups of the $T' \leftarrow T_1$ absorptions were also observed for all the other compounds studied here, though the $T' \leftarrow T_1$ absorption spectra of TIB-X with $X=4'\text{-CO-Ph}$, $4'\text{-CO}_2\text{CH}_3$, $3'\text{-CO-(2,4,6-(i-Pr)_3C}_6\text{H}_2)$ have another characteristic bands similar to those of benzophenone and 2-methylbenzophenone (Fig. 3).

The $T' \leftarrow T_1$ absorptions of TIB-X with $X=4'\text{-CO-Ph}$, $4'\text{-CO}_2\text{CH}_3$, and $4'\text{-CN}$ decayed following a single

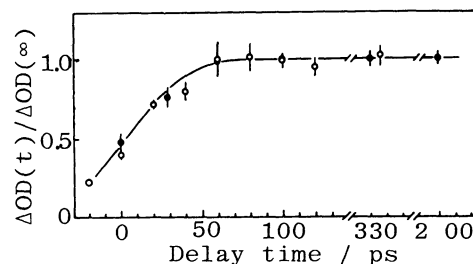


Fig. 2. Time evolution of $T' \leftarrow T_1$ absorption of TIB-H (●) and 2-methylbenzophenone (○). The smooth curve is the instrumental response function.

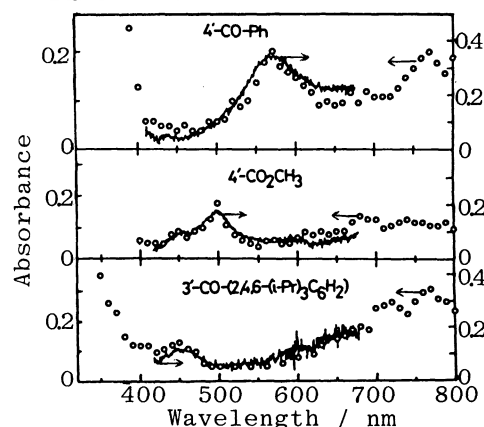


Fig. 3. $T' \leftarrow T_1$ absorption spectra of TIB-X at 2 ns (—) and 125 ns (○).

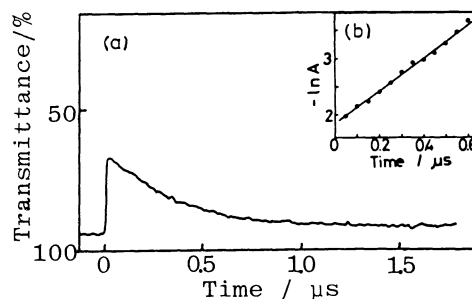


Fig. 4. Oscilloscope trace of the transmittance of the transient absorption of TIB-H at 700 nm (a). (b) is the first order plots.

exponential function on the microsecond time scale and no new absorptions were observed during the decay. However, for TIB-X with X=H, 4'-CH₃, 4'-Bu^t, 3'-CO-Ph, and 3'-CO-(2,4,6-(i-Pr)₃C₆H₂), we obtained different results. A typical example for TIB-H is shown in Figs. 4-6. By the nanosecond photolysis, the T'+T₁ absorption appeared within the duration of a laser pulse and the intensities above 430 nm decayed following a single exponential function with lifetime of 0.33 μs (Fig. 4), while those below 400 nm increased and reached a maximum value at 1 μs delay, followed by the decrease with two decay components as shown in Fig. 5. The rise time was 0.30 μs, and decay times of the short-lived and long-lived components were 6.74 μs and 46 ms, respectively. The transient spectra taken at delay times of 1.6 and 49 μs (Spectra A and B in Fig. 6) are different from the T'+T₁ absorption of TIB-H, and Spectrum A is identical to that of the 1,4-biradical observed by Hayashi et al.²⁾

Based on the above results, it is reasonable to conclude as follows: (1) The decay constant which was obtained from a single exponential decay of the absorptions above 430 nm reflects the triplet lifetime of TIB-H. (2) The absorption which builds up with a time constant of 0.30 μs and decays with a lifetime of 6.74 μs is due to the 1,4-biradical. (3) The long-lived component may be assigned to the dienol which is produced via the 1,4-biradical, though the

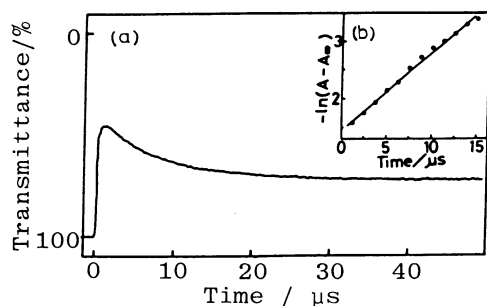


Fig. 5. Oscilloscope trace of the transmittance of the transient absorption of TIB-H at 370 nm (a). (b) is the first order plots.

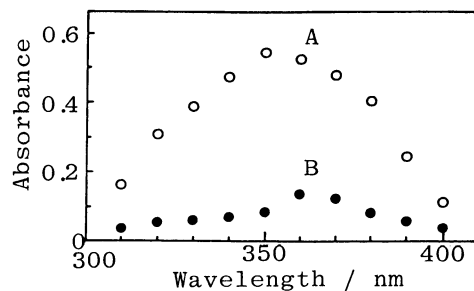


Fig. 6. Transient absorption spectra of TIB-H at 1.6 (A) and 49 μs (B).

Table 1. Time constants for the triplet states of TIB-X and the 1,4-biradicals

Compounds	Triplet life times/μs	Biradical	
		buildup times/μs	decay times/μs
-H	0.33±0.01	0.30	6.74±0.11
4'-CO-Ph	0.38±0.02	—	—
4'-CO ₂ CH ₃	0.45±0.01	—	—
4'-CH ₃	0.18±0.01	0.18±0.01	5.10±0.78
4'-Bu ^t	0.17±0.02	0.17±0.01	4.35±0.21
4'-CN	0.33±0.03	—	—
4'-OCH ₃	0.15±0.01	?	?
3'-CO-Ph	0.48±0.03	0.47±0.05	7.1±0.5
3'-CO-(2,4,6-(i-Pr) ₃ C ₆ H ₂)	0.56±0.06	0.61±0.05	8.43±0.65

lifetime of 46 ms is longer than that of trans-dienol observed upon the photolysis of 2-methylbenzophenone, i.e., 8 ms,¹⁰⁾ and Spectrum B is not so much different from Spectrum A in the spectral shape.

In Table 1, the triplet lifetimes of TIB-X and the buildup and decay times of the 1,4-biradicals are listed. It can be seen that the triplet lifetime of TIB-X is nearly equal to the buildup time of the 1,4-biradical in each compound with X=H, 4'-CH₃, 4'-Bu^t, 3'-CO-Ph, and 3'-CO-(2,4,6-(i-Pr)₃C₆H₂).

For the compounds with X=4'-CO-Ph, 4'-CO₂CH₃, and 4'-CN, no transient absorptions due to the 1,4-biradicals were observed. This may indicate that the intersystem crossing from the triplet to ground states competes with the biradical formation. This conclusion is consistent with the experimental fact that the quantum yields for cyclobutenol formation are 0.16 (X=4'-CO-Ph), 0.15 (X=4'-CO₂-CH₃), and 0.06 (X=4'-CN), while those for the compounds with X=H, 4'-CH₃, 4'-Bu^t, 3'-CO-Ph, and 3'-CO-(2,4,6-(i-Pr)₃C₆H₂) are 0.60, 0.48, 0.43, 0.64, and 0.79, respectively.^{1,4,5)}

We have presented that the 1,4-biradicals are produced via the triplet states of 2,4,6-triisopropylbenzophenones and the 1,4-biradicals convert to the cyclobutenols and dienols. The dienols probably reketonize to the original ketones. For the compounds with the small quantum yields of cyclobutenol formation, the intersystem crossing from the triplet to ground states may also participate in the nonradiative processes of the lowest triplet states.

References

- 1) Y. Ito, Y. Umehara, Y. Yamada, and T. Matsuura, J. Chem. Soc., Chem. Commun., 1980, 1160.
- 2) H. Hayashi, S. Nagakura, Y. Ito, and T. Matsuura, Chem. Lett., 1980, 939.
- 3) Y. Ito, H. Nishimura, T. Matsuura, and H. Hayashi, J. Chem. Soc., Chem. Commun., 1981, 1187.
- 4) Y. Ito, B.P. Giri, M. Nakasuji, T. Hagiwara, and T. Matsuura, J. Am. Chem. Soc., 105, 1117 (1983).
- 5) Y. Ito, H. Nishimura, Y. Umehara, Y. Yamada, M. Tone, and T. Matsuura, J. Am. Chem. Soc., 105, 1590 (1983).
- 6) Y. Ito and T. Matsuura, J. Am. Chem. Soc., 105, 5237 (1983).
- 7) K. Hamanoue, T. Hidaka, T. Nakayama, and H. Teranishi, Chem. Phys. Lett., 82, 55 (1981).
- 8) K. Hamanoue, K. Yokayama, Y. Kajiware, K. Nakajima, T. Nakayama, and H. Teranishi, Chem. Phys. Lett., 110, 25 (1984).
- 9) K. Hamanoue, K. Nakajima, T. Hidaka, T. Nakayama, and H. Teranishi, Laser Chem., 4, 287 (1984).
- 10) T. Nakayama, K. Hamanoue, T. Hidaka, M. Okamoto, and H. Teranishi, J. Photochem., 24, 71 (1984).
- 11) R.W. Anderson, Jr., R.M. Hochstrasser, H. Lutz, and G.W. Scott, J. Chem. Phys., 61, 2500 (1974); Chem. Phys. Lett., 28, 153 (1974).

(Received July 18, 1984)