The Laser-flash Photolysis of Propanone, Butanone, and 2-Pentanone. Study of Triplet Decay Processes in Aliphatic Carbonyl Compounds

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The laser-flash photolysis of propanone, butanone, and 2-pentanone were carried out in dichloromethane (265 nm, 15 ns flash duration). The emission spectra (fluorescence, phosphorescence, and P-type delayed fluorescence) and the transient absorption spectra (triplet state and acetyl radical) were recorded. From the decays of the emission and the absorption, the unimolecular (triplet decay) and bimolecular (T-T annihilation and self quenching) reaction-rate constants were determined. Oxygen quenched the triplet states with a diffusion-controlled rate constant (k_{O_2}=*ca.* $3\times10\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$).

Photochemical processes induced by stationary irradiation of aliphatic carbonyl compounds have been studied before in the absence and presence of quenchers.

Recently, the triplet state of propanone was investigated in detail by the use of tetramethyl-1,2-dioxetane (Chemiluminescence technique).1)

In the flash photolysis studies of propanone, triplet-triplet absorption and phosphorescence spectra were recorded at wavelengths longer than λ=300 nm by Porter *et al.*2) In these studies the ketyl radical formed from the triplet propanone was also detected.3)

In the laser-flash photolysis of 2-hexanone, 5-methyl-2-hexanone, and poly(3-buten-2-one), triplet 1,4-biradical intermediates produced by a Norrish Type II reaction were detected recently.4) In the photolysis of 3,3-dimethyl-2-butanone, poly(4,4-dimethyl-1-penten-3-one), and poly(3-methyl-3-buten-2-one), on the other hand, only radicals produced by α-cleavage in a Type I reaction were detected.4) The triplet lifetimes of propanone, butanone, and 2-pentanone were reported to be relatively long [τ_T=47 μs,4) 0.94 μs,5) (propanone), 13 μs, (butanone in gas phase),6) 77 ns,7) and 240 ns (in the gas phase)8) (2-pentanone)].

This paper reports on studies concerning the 265 nm laser-flash photolysis of propanone, butanone, and 2-pentanone carried out in dichloromethane solution in order to elucidate the physical and chemical deactivation processes of the triplet aliphatic carbonyl compounds.

Experimental

Materials. The propanone, butanone, and 2-pentanone were dried on sodium sulfate and distilled twice using a split-tube column.

The dichloromethane (for fluorescence spectroscopy) was washed five times with a 5% sodium carbonate solution and five times with distilled water. After drying on anhydrous calcium chloride, the dichloromethane was distilled twice using the split-tube column.

The acetonitrile (for spectroscopy) was refluxed five times on diphosphorus pentaoxide and distilled twice using the split-tube column.

The hexane (for fluorescence spectroscopy) was washed five times with sulfuric acid and five times with distilled water. After drying on anhydrous calcium chloride and calcium hydride, the solvent was distilled twice using the split-tube column.

The methanol (for spectroscopy) was refluxed with magnesium methoxide for eight hours and distilled twice using the split-tube column.

Apparatus. The flash photolysis system consisting of a Nd-laser has been described before (265 nm, 15 ns flash length).9) The output of the laser and the intensity of the incident laser light were determined by means of the cycloreversion reaction of *r*-1,*t*-2,*t*-3,*c*-4-tetraphenylcyclobutane in 1-chlorobutane (ϕ=0.34).10) The transient absorptions were measured using a pulsed Xenon lamp (Osram XBO 450 W). For the emission measurements a gating system was used.11) This system protected the highly sensitive photomultiplier (RCA 78-35) from the strong emission during and immediately after the flash. The gating times of 1—2 μs (propanone) and 100—200 ns (butanone and pentanone) were applied. At the wavelengths longer than λ=400 nm, filters (Schott, BG 23, GG 455, *etc.*) were used. By choosing an appropriate concentration of the solute (3×10^{-2} mol dm^{-3}), the absorbance at λ=265 nm was kept at 0.5. After the solutions were filled in rectangular cells (optical length: 1.0×10^{-2} m) they were saturated with purified argon and, then, the laser-flash photolyis was carried out. The O_2 impurity of the argon gas was estimated to be less than 1×10^{-1}%. The emission and the absorption spectra were normalized with respect to an incident intensity of 2.0×10^{-8} einstein per flash.

Results and Discussion

1. Emission Spectra. During and immediately after the flash, a strong emission was detected in the wavelength range of 300—500 nm. The spectrum exhibited an emission maximum at λ=400 nm which agrees with the reported maximum of the fluorescence spectrum.12)

Figure 1 shows time-resolved emission spectra monitored several microseconds after the flash by using the gating system [monitored at 6, 8, and 10 μs (propanone), 1.0, 1.5, 2.0, and 2.5 μs (butanone), 0.8, 1.0, 1.2, and 1.6 μs (2-pentanone)]. The emission spectrum, first-recorded, possesed the maximum in the wavelenth range of 410—430 nm. The maximum shifted to longer wavelengths with the lapse of the time after the flash. The spectra of butanone recorded at 2.0 μs and of 2-pentanone recorded at 1.2 μs at after the flash had two maxima, at λ=410 and 445 nm. Since the excited singlet lifetimes of these compounds have been reported to be much shorter than the time range investi-

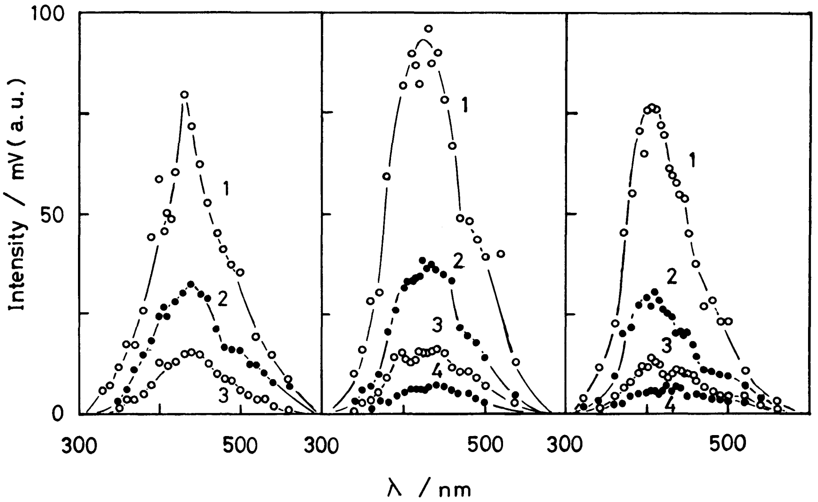

Fig. 1. Time-resolved emission spectra of propanone, butanone, and 2-pentanone in dichloromethane (3.0×10^{-2} mol dm^{-3}) recorded with the aid of a gating system. Time of recording: a) (propanone) 6 (1), 8 (2), and 10 (3) μs; b) (butanone) 1.0 (1), 1.5 (2), 2.0 (3), and 2.5 (4) μs; c) (2-pentanone) 0.8 (1), 1.0 (2), 1.2 (3), and 1.6 μs after the flash. The spectra were normalized with respect to an incident intensity of 2×10^{-8} einstein per flash.

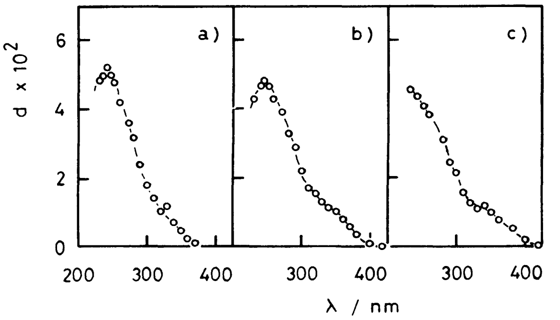

Fig. 2. Transient absorption spectra of propanone, butanone, and 2-pentanone monitored immediately after the flash in dichloromethane solution (3.2×10^{-2} mol dm^{-3}). a: propanone; b: butanone; c: 2-pentanone. The spectra were normalize with respect to an incident intensity of 2×10^{-8} einstein per flash.

gated here,[13] it seems that the observed emission is due to the P-type delayed fluorescence and the phosphorescence. On this basis, the spectra recorded latest are attributed to the phosphorescence. Indeed, they agree with the phosphorescence spectra reported in the literature.[14]

2. Absorption Spectra of the Transient Species. The absorption spectra of transient species monitored immediately after the flash are shown in Fig. 2. The spectra exhibit an absorption maximum at λ=240 nm (propanone), at λ=245 nm (butanone), and at a wavelength shorter than 240 nm (2-pentanone). These transient absorption spectra are assigned to triplet-triplet absorption on the basis of the decay rate, which corresponds to the rate of the decay of the long-lived emission (*vide ante*).

Figure 3 presents absorption spectra of long-lived species, recorded at 14 μs (propanone), 7 μs (butanone), and 2 μs (2-pentanone). The spectra which have maxima around 320 nm and at λ=560 nm resemble strongly the spectrum of the acetyl radical reported by Noda *et al.*[15] Therefore, they are assigned to acetyl radicals. The generation of acetyl radical is feasible, in the present case, in terms of the generally accepted mechanism that the α-cleavage reaction is an important route in the deactivation of the triplet states of the carbonyl compounds.

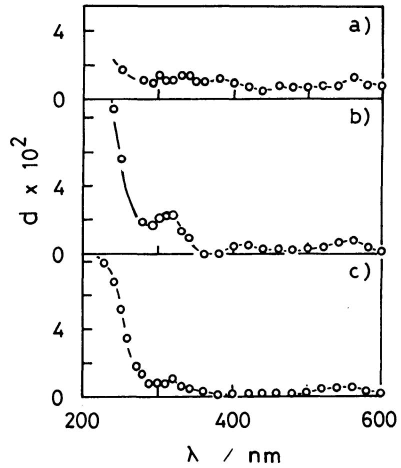

Fig. 3. Transient absorption spectra of the long-lived species of propanone (a), butanone (b), and 2-pentanone (c) in dichloromethane solution (3.2×10^{-2} mol dm^{-3}) recorded at 14(a), 7(b), and 2(c) μs after the flash. The spectra were normalized with respect to an incident intensity of 2×10^{-8} einstein per flash.

3. Decay of the Transient Absorption and Emission. Figure 4 presents oscilloscope traces depicting the decay. The decays of both the absorption and the emission obeyed first-order kinetics. Whereas the decay rate ($k_{\text{meas.}}$) of the transient absorption was constant at all wavelengths monitored, the $k_{\text{meas.}}$ value of the emission depended on the wavelength. Figure 5 shows the effect of the laser light intensity on the $k_{\text{meas.}}$ value, obtained by means of the decay of the absorption at λ=250 nm and those of the emissions at λ=360 and

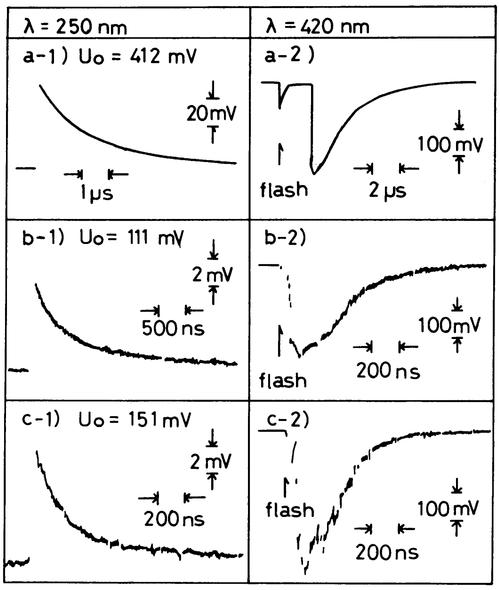

Fig. 4. Typical oscilloscope traces illustrating changes of the absorption (1) and the emission (2) of propanone (a), butanone (b), and 2-pentanone (c) in dichloromethane solution (3.0×10^{-2} mol dm^{-3}). Monitored at wavelength: λ=250 nm (absorption) and 420 nm (emission), flashed photons (10^{-8} einstein per flash): 2.0 (a-1), 2.2 (a-2), 1.0 (b-1), 1.4 (b-2), 0.8 (c-1), and 1.0 (c-2).

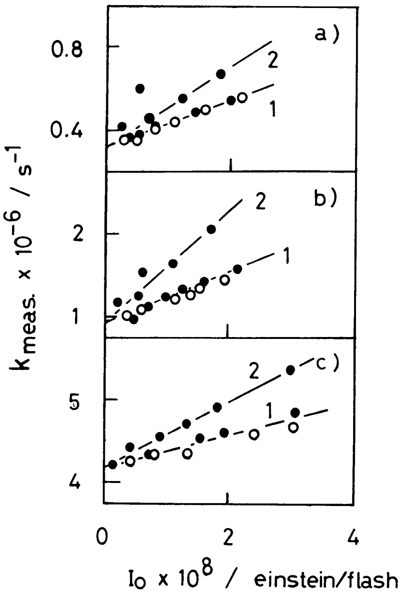

Fig. 5. The plot of the $k_{meas.}$values as a function of the flashed photons. a: propanone; b: butanone; c: 2-pentanone in dichloromethane solution (3×10^{-2} mol dm^{-3}). Curve 1: absorption at λ= 250 nm and emission at λ=500 nm. Curve 2: emission at λ=360 nm.

500 nm. The two emission wavelengths were chosen with the intention to discriminate, possibly, delayed fluorescence from phosphorescence. It can be seen from Fig. 5, $k_{meas.}$ value increased linearly with the incident intensity, I_0, which is proportional to the quantity of the absorbed photons. This behavior is indicative for triplet-triplet annihilation. Actually, the same linear relationship between the $k_{meas.}$ value an I_0 was found for the decay of the absorption at all wavelengths and the decay of the emission at λ=500 nm (straight line 1, in Fig. 5). On the other hand, a slope about twice that of straight line 1 was found for straight line 2, obtained by monitoring the decay of the delayed fluorescence at λ=360 nm. As a matter of fact, the decay rate constant of the P-type delayed fluorescence should be twice as large as the triplet decay rate constant. These results confirm the assumed attribution of the transient absorption spectrum recorded immediately at the end of the flash to the triplet states.

4. Dependence of the Triplet Decay Rate on the Absorbed Photons. In a simplified way, the triplet decay can be considered being due to two Reactions, 1 and 2;

$$T_1 \xrightarrow{\Sigma k'} S_0, \qquad (1)$$

$$T_1 + T_1 \xrightarrow{k'_{T-T}} 2\,S_0, \qquad (2)$$

where $\sum k'$, and k'_{T-T} are the apparent rate constants of all first order (including self-quenching) and second-order (T–T annihilation) processes respectively. The rate of the triplet decay is given by Eq. 3:

$$-\frac{d[T]}{dt} = \Sigma k'[T] + k'_{T-T}[T]^2, \qquad (3)$$

By dividing both sides of Eq. 3 by [T], the triplet concentration, Eq. 4 is obtained:

$$-\frac{d[T]}{[T]dt} = \Sigma k' + k'_{T-T}[T]. \qquad (4)$$

The left side of Eq. 4 can be transformed into $[-d(\ln[T])/dt\ (\equiv k_{meas.})]$. Figure 5 shows that the $k_{meas.}$ values is directly proportional to I_0. The initial triplet concentration, $[T]_0$, is obtained from I_0 using a quantum yield of the intersystem crossing, $\phi_{ic}=1.0$ (propanone[5] and butanone[6]) and 0.63 (2-pentanone).[7]

The experimental decay rate constant, $k_{meas.}$ is expressed by Eq. 5:

$$k_{meas.} = \Sigma k' + k'_{T-T}[T]_0. \qquad (5)$$

Figure 6 shows the plots of the $k_{meas.}$ values, determined by the absorption measurements at various initial concentrations of the carbonyl compounds ($[S_0]$), *vs.* $I_{abs.}$, which is proportional to $[T]_0$. For all initial concentrations of the carbonyl compound, the plots yielded straight lines being parallel to each other.

As far as the T–T annihilation is concerned, it has to be taken into account that two pathes are possible as is shown below;

$$T_1 + T_1 \begin{cases} \xrightarrow{\alpha} S_1^* + S_0, & (6a) \\ \xrightarrow{(1-\alpha)} 2\,S_0. & (6b) \end{cases}$$

Here, α denotes the portion of the triplet states reacting accordig to Reaction 6a which regenerates the triplet state *via* the intersystem crossing ($S_1^*\rightarrow T_1$). This process occurs rather rapidly, *i.e.* the singlet lifetime (∠10 ns[13]) is much shorter than the triplet lifetime. Consequently, the apparent rate constant, k'_{T-T}, is related to the rate constant of the T–T annihilation, k_{T-T}, according to Eq. 7:

Table 1. Triplet decay rate constants $\sum k_T$, and rate constants of triplet-triplet annihilation, k_{T-T}, and self-quenching k_{self}.

Compound	$\sum k_T \times 10^{-6}$	$k'_{T-T} \times 10^{-9}$	$k_{self.} \times 10^{-6}$
	s^{-1}	$dm^3\ mol^{-1}$	s^{-1}
Propanone	0.16	3	3
Butanone	0.73	7	6
2-Pentanone	3.8	6	6

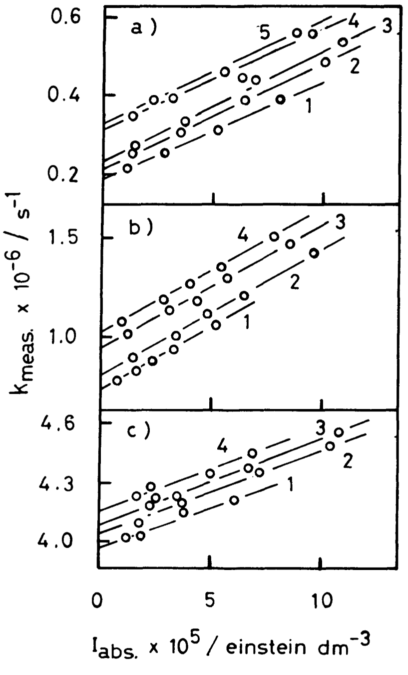

Fig. 6. The triplet decay rate, $k_{meas.}$, as a function of the absorbed photons per flash observed with the ketone solutions of various concentration in dichloromethane. a: [propanone]=1.3 (1) 2.0 (2), 2.6 (3), 5.2 (4), and 6.5 (6)$\times 10^{-2}$ mol dm^{-3}; b: [butanone]= 0.7 (1), 2.1 (2), 4.2 (3), and 5.6 (4)$\times 10^{-2}$ mol dm^{-3}; c: [2-pentanone]=0.7 (1), 1.4 (2), 2.0 (3), and 3.4 (4)$\times 10^{-2}$ mol dm^{-3}.

$$k'_{T-T} = (1-\alpha\phi_{ic}/2)\,k_{T-T}. \qquad (7)$$

The values of k'_{T-T}, obtained from the slope of the straight lines in Fig. 6, are listed in Table 1. Because α is not known, the values of k_{T-T}, could not be calculated.

5. Self-quenching. The intercept of the straight lines in Fig. 6 corresponds to the values of $\sum k'$, in Eq. 5. The plots of $\sum k'$, obtained with the three carbonyl compounds, *vs.* the carbonyl concentration are shown in Fig. 7. The straight lines observed reflect the dependence of $\sum k'$, on the carbonyl concentration according to Eq. 8;

$$\sum k' = \sum k_T + k_{self.}[S_0], \qquad (8)$$

where $k_{self.}$ is the rate constant of the self-quenching reaction: $S_0 + T_1 \rightarrow S_0 + S_0$ and $\sum k_T$ is the sum of all the first-order rate constants. The values of $\sum k_T$ and $k_{self.}$ obtained from the intercept and the slope of the straight lines in Fig. 7 are given in Table 1. The $\sum k_T$ values found with propanone and butanone are

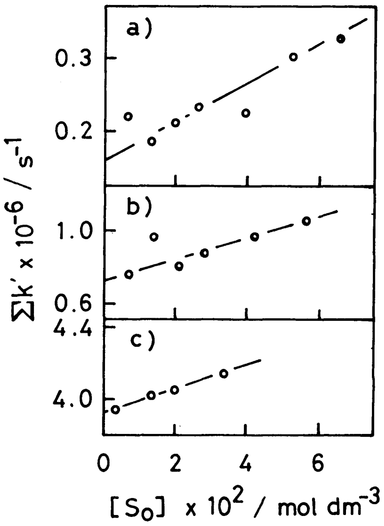

Fig. 7. Plots of the k', values *vs.* the initial carbonyl concentrations. a: propanone; b: butanone; and c: 2-pentanone.

Table 2. Decay rate constants of the triplet states in various solvents and quenching-rate constant of oxygen

Compound	Solvent	$k_{meas.} \times 10^{-6,a)}$	$k_{meas.O_2} \times 10^{-7,a)}$	$[O_2] \times 10^3$	$k_{O_2} \times 10^{-10}$
		s^{-1}		$mol\ dm^{-3}$	$dm^3\ mol^{-1}\ s^{-1}$
Propanone	CH_2Cl_2	0.55	6.0	*ca.* 2$^{b)}$	*ca.* 3
	CH_3CN	0.41	7.0	1.3$^{c)}$	5.4 ?
	CH_3OH	0.37	8.8	2.1$^{d)}$	4.2
	C_6H_{14}	1.2	7.9	3.1$^{d)}$	2.5
Butanone	CH_2Cl_2	2.0	5.9	*ca.* 2$^{b)}$	*ca.* 3
	CH_3CN	2.0	5.8	1.3$^{c)}$	4.3 ?
	CH_3OH	2.0	6.1	2.1$^{d)}$	2.8
	C_6H_{14}	3.5	*ca.* 11	3.1$^{d)}$	3.4
2-Pentanone	CH_2Cl_2	4.5	5.7	*ca.* 2$^{b)}$	*ca.* 3
	CH_3CN	4.2	4.6	1.3$^{c)}$	3.2
	CH_3OH	4.1	6.4	2.1$^{d)}$	2.9
	C_6H_{14}	—	*ca.* 11	3.1$^{d)}$	3.4

Concentrations of carbonyl compounds: 3.0×10^{-2} mol dm^{-3}. Flashed photons: 2.0×10^{-8} einstein per flash, a) pseudo first order rate constants (error limit: ±20%), b) Ref. 17, c) Ref. 18, d) Ref. 19.

greater than the values previously reported [$\sum k_T = 2.1\times10^4\ s^{-1}$ (propanone in acetonitrile)[2] and $7.7\times10^4\ s^{-1}$ (butanone in the gas phase)[6]]. The $k_{self.}$ value is in the order of $10^6\ dm^3\ mol^{-1}\ s^{-1}$.

6. Reaction of Triplets with Molecular Oxygen. Oxygen was found to quench the triplet states very effectively. Rate constants, k_{O_2}, were determined by measuring the triplet decay rate in O_2-saturated solution ($k_{meas.O_2}$) by using Eq. 9:

$$k_{meas.O_2}=k_{meas.}+k_{O_2}[O_2]. \tag{9}$$

As can be seen from Table 2, $k_{O_2}=(3.0\pm1.5)\times10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ was found, *i.e.* the reaction of O_2 with the triplet states of the carbonyl compounds under investigation is encounter-controlled.

7. Solvent Effects. Three additional solvents were used in this work besides dichloromethane; acetonitrile, methanol, and hexane. As can be seen from Table 2, $k_{meas.}$ value is the same within the error limit, except for hexane. The hydrogen abstraction reaction, presumable, becomes important in hexane and thus leads to faster triplet decay rates.

Conclusion

Propanone, butanone, and 2-pentanone were irradiated in dilute solution at room temperature with 15 ns flashes of 265 nm light. The absorption and emission measurements were carried out. The T–T absorption, prompt and the P-type delayed fluorescence, and the phosphorescence were observed. The rate constants of the T–T annihilation and the self-quenching were measured. The k'_{T-T} (*ca.* $5\times10^9\ dm^3\ mol^{-1}\ s^{-1}$) was found to be about four times lower than in the case of benzophenone.[20] This difference might be indicative for the fact that a significant portion of the T–T annihilation reactions regenerate the triplet states *via* $T_1+T_1\rightarrow S_1^*+S_0$, following by $S_1^*\rightarrow S_0$. The self-quenching rate constans are much higher than the value reported for propanone ($10^3\ dm^3\ mol^{-1}\ s^{-1}$).[21] Actually, the present values lie in the range of 10^5 to $10^7\ dm^3\ mol^{-1}\ s^{-1}$ pertaining to aromatic carbonyl compounds such as acetophenone and benzophenone.[20]

It appears, that in the case of propanone and butanone the α-cleavage reaction is the most important chemical deactivation process for the triplet states. The same holds for 2-pentanone, despite the fact that the α-hydrogen abstraction leading to the triplet 1,4-biradicals is feasible in this case.

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