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NATURE OF THE EXCITED TRIPLET STATES IN THE PHOTOLYSIS OF O-ACYLOXIMES

Masayuki YOSHIDA, Hirochika SAKURAGI, Toshihiro NISHIMURA,
Shun-ichi ISHIKAWA, and Katsumi TOKUMARU*
Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113
*Institute of Chemistry, The University of Tsukuba,
Sakura-mura, Ibaraki-ken 300-31

The triplet states of O-acyl aromatic ketoximes, $RCO_2N{=}CR_1R_2$ (I, II, and III), undergo homolytic cleavage into iminyl radicals, $R_1R_2C{=}N\cdot$, and acyloxyl radicals, $RCO_2\cdot$. The triplet states have their excitation energies which are close to those of their parent ketones, $R_1R_2C{=}O$, and are abundant in π,π^* character. The excitation energies are dissipated through cleavage of the N-O bonds.

Although photochemistry of azomethine compounds has been a subject of much recent effort,$^{1)}$ there have been very few reactions which proceed certainly from their excited states. O-Acyloximes have previously been shown to be photochemically cleaved into iminyl and acyloxyl radicals from their excited states.$^{2)}$ We now wish to report that their homolytic cleavage takes place from the triplet states, which have comparable excitation energies to those of their parent ketones and are rich in π,π^* character as the results of an examination of the effect of sensitizers on their decomposition, measurements of their ability to quench the phosphorescence from aromatic ketones at room temperature, and observations of their phosphorescence at 77K. To our knowledge, this report provides the first quantitative estimation of the energy of the reactive triplet state of azomethine compounds.

In the first place, an effect of sensitizers and quenchers on the decomposition of O-acyloximes (I, II, and III) was examined. The O-acyloximes were irradiated in benzene under nitrogen atmosphere either in the presence or in the absence of sensitizers or quenchers with a 1000 W high pressure mercury lamp surrounded with Toshiba

UV-D1B glass filters which transmit 366 nm light, and the consumption of the acyloximes was followed by nmr. The typical results for benzophenone O-phenylacetyloxime (Ia) are depicted in Figure 1, and the summarized results are shown in Table 1.

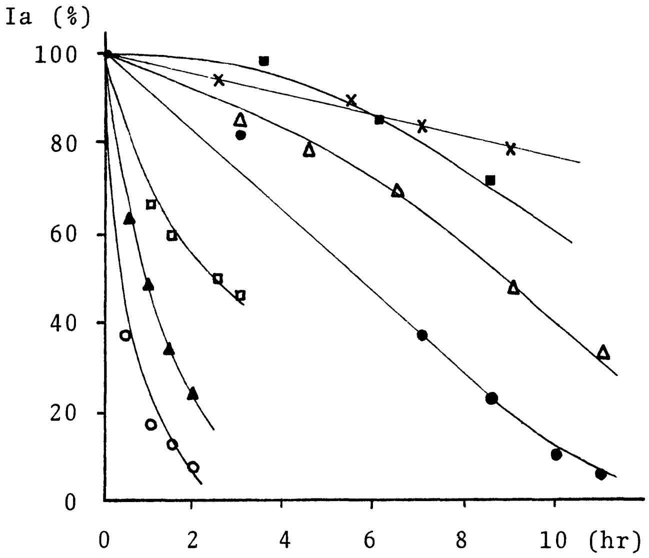
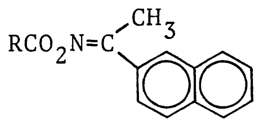


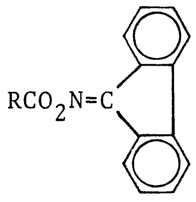
Figure 1. Photolysis of Ia (0.1 M) in benzene under nitrogen atmosphere. The sensitizers and the quencher employed and their concentrations (M) were as follows: nil(•); xanthone(▲), 0.036; benzophenone(○), 0.1; 2-acetonaphthone (□), 0.35; benzil(△), 0.1; fluorenone(■), 0.026; 1,3-pentadiene(×), 0.13.[3]

$RCO_2N{=}C(C_6H_5)_2$

Ia, R = $C_6H_5CH_2$; Ib, R = CH_3;
Ic, R = C_6H_5; Id, R = $4\text{-}CH_3OC_6H_4$



II, R = $4\text{-}CH_3C_6H_4$



IIIa, R = CH_3; IIIb, R = $4\text{-}CH_3C_6H_4$;
IIIc, R = C_6H_5

$CH_3ON{=}C(C_6H_5)_2$ IV

Figure 1 indicates that the decomposition of Ia was considerably accelerated by an addition of the sensitizers with higher triplet energies such as xanthone (74.1 kcal/mol) and benzophenone (68.6 kcal/mol) and moderately accelerated by 2-acetonaphthone (59.4 kcal/mol), but rather retarded by the sensitizers with lower triplet energies such as benzil (53.4 kcal/mol) and fluorenone (53.3 kcal/mol). The decomposition was effectively quenched by 1,3-pentadiene. Therefore, it is clear that the triplet aromatic ketones with high excitation energies are effective to sensitize the decomposition of the acyloxime occuring from the triplet state and the efficiency of the energy transfer tends to decrease with the decrease of the triplet energies of the sensitizers employed.

Table 1. Effect of Sensitizers on Decomposition of O-Acloximes in Benzene

Sensitizers	O-Acyloximes				
(E_T[4,5] in kcal/mol)	Ia	Ib	II	IIIa	IIIb
Xanthone (74.1)	++	++			
Benzophenone (68.6)	++	++	++	++	++
2-Acetonaphthone (59.4)	+		++		
Benzil (53.4)	–	–	+		
Fluorenone (53.3)	–		+	+	+

Symbols, ++, +, and –, denote noticeable, moderate, and slightly negative accelerations on the decomposition, respectively.

Benzophenone O-acetyloxime (Ib) was also readily decomposed by sensitization with xanthone and benzophenone, whereas benzil did not sensitize the decomposition. Decomposition of 2-acetonaphthone O-(4-methylbenzoyl)oxime (II) was easily effected by benzophenone and 2-acetonaphthone, but slightly effected by fluorenone and benzil. For fluorenone O-acetyloxime (IIIa) and O-(4-methylbenzoyl)oxime (IIIb), benzophenone noticeably accelerated the decomposition, whereas fluorenone slightly accelerated the decomposition. The above results show that the photolysis of the acyloximes is sensitized by their corresponding parent ketones or ketones with triplet energies higher than those of the parent ketones. Thus, it is suggested that the triplet energies of the acyloximes are close to those of the parent ketones.

In the second place, to ascertain quantitatively the above estimation on the energy transfer process an ability of the acyloximes to quench the phosphorescence emitted from benzophenone, 2-benzoylnaphthalene, and benzil in deaerated carbon tetrachloride at room temperature was examined.6) The Stern-Volmer plots of the reciprocals of relative phosphorescence intensities, I_p^o/I_p, against concentrations, [Q], of the acyloximes gave a linear relationship with a slope of $k_q\tau_T$: $I_p^o/I_p = 1 + k_q\tau_T[Q]$, where k_q denotes the rate constant for the quenching process and τ_T means the lifetime of the triplet state of the ketones in the absence of the acyloximes at room temperature, and the results are summarized in Table 2. To determine the triplet lifetimes of these ketones, trans-stilbene was employed as a standard substrate to quench the phosphorescence of these ketones in carbon tetrachloride, since the rate constants are known for the quenching of the triplet states of these ketones by trans-stilbene at room temperature.[7,8] The measured $k_q\tau_T$ values for stilbene in carbon tetrachloride were divided by reported k_q values to determine τ_T values for the present ketones;[9] τ_T values for benzophenone, 2-benzoylnaphthalene, and benzil are 0.82×10^{-5}, 3.8×10^{-5}, and 3.9×10^{-5} sec, respectively. The observed $k_q\tau_T$ values for the acyloximes are divided by the above τ_T values and the resulting k_q values are listed in Table 2.

Table 2. Quenching of Phosphorescence from Ketones by Acyloximes in Carbon Tetrachloride at Room Temperature

	Phosphors (E_T,[4] kcal/mol)					
	Benzophenone (68.6)		2-Benzoylnaphthalene (59.6)		Benzil (53.4)	
Quenchers	$k_q\tau_T \times 10^{-4}$ (M^{-1})	$k_q \times 10^{-9}$ ($M^{-1}sec^{-1}$)	$k_q\tau_T \times 10^{-4}$ (M^{-1})	$k_q \times 10^{-9}$ ($M^{-1}sec^{-1}$)	$k_q\tau_T \times 10^{-4}$ (M^{-1})	$k_q \times 10^{-9}$ ($M^{-1}sec^{-1}$)
Ia	2.6	3.2				
Ib	2.2	2.7				
Ic	2.2	2.7	2.2	0.59	0.007>	0.002>
II	4.9	6.0	25	6.7	0.6	0.15
IIIa	5.8	7.1				
IIIc	7.3	9.0	40	10.7	5.0	1.3
IV	3.3	4.1				
Stilbene	5.3	6.5[7]	33	8.8[7]	7.0	1.8[8]

Table 2 indicates that for the respective triplet ketones k_q values tend to increase as the oxime moiety of the acyloximes changes from benzophenoxime (I) to 2-acetonaphthoxime (II) and fluorenoxime (III) and that for the respective acyloximes k_q values are least for benzil among three triplet ketones examined. It is generally accepted that triplet energy transfer to a quencher proceeds with a diffusion-controlled rate constant (11×10^9 $M^{-1}sec^{-1}$ in carbon tetrachloride at 25°C),[10] when a sensitizer has a triplet excitation energy more than 3 kcal/mol higher than that of the quencher. The rate constants begin to decrease when the triplet energy of a sensitizer is lowered nearly to that of the quencher and further tend to decrease with the decrease in the triplet energies of sensitizers.[11] Fluorenone O-benzoyloxime (IIIc) quenches triplet benzophenone and 2-benzoylnaphthalene with near diffusion-controlled rate constants, but a quenching rate constant of triplet benzil is about one seventh of the diffusion-controlled one.

This result suggests that the triplet energy of IIIc is close to that of benzil and 3 kcal/mol or more lower than that of 2-benzoylnaphthalene. A fact that II quenches triplet 2-benzoylnaphthalene with a near diffusion-controlled rate constant and triplet benzil with a far lower rate constant leads one to estimate that II is slightly lower in triplet energy than 2-benzoylnaphthalene. Similarly, the triplet energy of Ic is estimated to be close to that of benzophenone on the ground that Ic quenches triplet benzophenone with a rate constant slightly lower than the diffusion-controlled one, and 2-benzoylnaphthalene and benzil with much lower rate constants in this order.12)

In the quenching of triplet benzophenone by various acyloximes, magnitudes of the rate constants are mainly governed by the structure of oxime moiety of the acyloximes and are not dependent upon the acyl moieties among the acyloximes with the same oxime moiety. Furthermore, benzophenone O-methyloxime (IV) quenches triplet benzophenone with nearly the same rate constant as those for benzophenone O-acyloximes, Ia, Ib, and Ic.13) This fact suggests that the oxime moiety of the acyloximes functions to accept triplet excitation energies from sensitizers.

In the third place an attempt was undertaken to observe phosphorescence of the acyloximes in EPA at 77K. Phosphorescence of Ia, Ic, and Id was successfully observed, but phosphorescence of the other acyloximes was too weak to be recorded. It is noticeable that phosphorescence of I was observed in view that phosphorescence of azomethine compounds has never been observed except our previous findings on cyclic imines such as 1,3,3-triphenylisoindolenine (V) and 1-phenyl-3,4-dihydroisoquinoline (VI)14) and an acyclic imine, N-(4-dimethylaminobenzylidene)aniline.15) Measurement of phosphorescence spectra and their lifetimes of I showed the triplet energy to be 73, 69, and 71 kcal/mol and the triplet lifetime to be 0.1, 0.1 and 0.1 sec for Ia, Ic, and Id, respectively. The relatively long lifetimes of the triplet state are indicative of their high π,π^* character.

These results for triplet energies of I carrying diphenylmethaniminoxyl moiety are in contrast with our previous findings for the triplet energies of V and VI with the similar, though cyclic, diphenylmethaniminyl moiety, whose triplet state lies 61 or 54 kcal/mol above their ground state and is also abundant in π,π^* character.14) The comparison may suggest that the substitution of an oxygen atom on the nitrogen atom of the diphenylmethaniminyl moiety elevates their triplet energy in about 10 kcal/mol.

References and Notes

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3. The concentrations of added sensitizers were varied according to individual absorption coefficient of the sensitizer at 366 nm so that light quantities absorbed are all identical.
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6. A Hitachi fluorescence spectrometer MPF-2A was used.
7. W. D. K. Clark and C. Steel, J. Amer. Chem. Soc., 93, 6347 (1971).
8. W. G. Herkstroeter and G. S. Hammond, ibid., 88, 4769 (1966).
9. The present $k_q\tau_T$ values measured in carbon tetrachloride were divided by k_q values obtained in benzene or in iso-octane. However, this treatment is supposed not to give unreasonable conclusion, since viscosities of these solvents are not too much different.
10. Ref. 4, p. 55.
11. Ref. 5, p. 47.
12. Ic quenches phosphorescence from 2-benzoylnaphthalene (E_T, 59.6 kcal/mol) with a rate constant of twentieth of that for the quenching of phosphorescence from benzophenone (E_T, 68.6 kcal/mol). This value seems exceedingly higher than that would be expected on the decrease of the triplet energies of sensitizers (9 kcal/mol) in usual triplet excitation transfer processes. Similarly, Ia is not only sensitized by benzophenone but also moderately sensitized by 2-acetonaphthone in spite of a fact that the triplet energy for 2-acetonaphthone is nearly 10 kcal/mol lower than that of benzophenone. These results suggest that in addition to the usual triplet excitation transfer mechanism another mechanism such as excited complex mechanism might partly participate to the sensitization. The authors are grateful to the referee for his comment on this discussion.
13. This fact enables one to estimate that the triplet energy of IV is nearly the same with those of I's ($E_T \sim 70$ kcal/mol). The result is in harmony with Padwa's estimation for the triplet energy of syn-acetophenone O-methyloxime ($E_T \sim 72$ kcal/mol) [A. Padwa and F. Albrecht, J. Amer. Chem. Soc., 94, 1000 (1972)].
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