Quenching $Cd(^3P_1)$ Atoms by Ethylene Derivatives

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Recent studies have shown that the efficiency of olefins for quenching triplet benzene[1,2] and acetone[3] depends strongly on the number of substitution, *i. e.*, the efficiency of tetramethylethylene is more than ten times larger than that of ethylene. In $Hg(^3P_1)$-photosensitization, however, such a strong dependence has not been observed.[4] Two possible explanations are considered; one is the difference in energy transferred from a sensitizer to a quencher, the other is the difference in the electronic state of sensitizer. $Cd(^3P_1)$-photosensitization may provide an opportunity to give the answer, because Cd-atom is very similar to Hg-atom in the electronic property, but the energy transferred in $Cd(^3P_1)$-photosensitization (87.7 kcal) is much less than that in $Hg(^3P_1)$-photosensitization (112.7 kcal) and is close to those in benzene (84.4 kcal)[5] and acetone (~80 kcal)[6]-photosensitizations.

As stated in the previous paper,[7] 2-butene molecules isomerize between cis and trans forms efficiently by the Cd-photosensitization without decomposition and other type of isomerization. In the presence of other quenchers, the cis-trans isomerization of 2-butene is retarded, the rate of which may be expressed as follows,

$$R_0/R = 1 + (k_x/k_b)([X]/[B])$$

where, R and R_0 are the rate of isomerization of 2-butene in the presence and absence of other quencher X. k_x/k_b is the relative quenching efficiency of the quencher X to 2-butene B. In this experiment, *cis*-2-butene is used as a detector compound. The relative quenching efficiency, k_x/k_b, can now be evaluated in a straightforward manner from the plots of R_0/R *vs.* [X]/[B].

The results are summarized in Table 1 along with the values obtained by using $Hg(^3P_1)$ atoms,[4] triplet benzene[1,2] and acetone[3] as the sensitizer. Obviously, the trend obtained with $Cd(^3P_1)$ is very similar to that with $Hg(^3P_1)$. This suggests that the strong dependence observed in quenching triplet benzene and acetone is not due to the small amount of energy transferred in the photosensitized reaction.

TABLE 1. RELATIVE QUENCHING EFFICIENCIES

Quencher	$Cd(^3P_1)$		$Hg(^3P_1)$	Benzene		Acetone
	this work	ref. 8*	ref. 4*	ref. 1	ref. 2	ref. 3*
Ethylene	1.03±0.09	1.05	0.90	0.16±0.02	0.25	0.16
Propylene	1.18±0.04	1.06	0.93	0.51±0.04	0.47	0.33
1-Butene	1.08±0.09	1.16		0.50±0.04	0.51	0.33
cis-2-Butene	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)
Isobutene	1.11±0.03		0.95		1.27	0.66
Trimethylethylene	1.02±0.10			1.7±0.2	1.61	1.4
Tetramethyl-ethylene	0.99±0.11		0.95	3.0±0.3	2.63	8.7
Butadiene	1.13±0.04		0.93		15.	870.
Acetylene	1.03±0.03	0.96	0.83			0.015
Propane	~0	10^{-4}	0.045	~0		

* These values were obtained by a physical method of measuring the quenching of the phosphorescence.

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