BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 329—333 (1969)

The Efficiencies of Hydrocarbons and Hydrogen in Quenching Triplet Cadmium Atoms

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(Received June 11, 1968)

The relative efficiencies of sixteen hydrocarbons and of hydrogen in quenching triplet cadmium atoms have been measured at 270±1°C by the competitive quenching method, using the cadmium-photosensitized *cis-trans* isomerization of *cis*-2-butene as a detector reaction. The quenching efficiencies of all the olefins studied and of acetylene were almost the same. The efficiencies of saturated hydrocarbons were, however, very low compared with those of unsaturated ones. Hydrogen was as efficient as unsaturated hydrocarbons.

Electronic energy-transfer reactions in the gas phase are of fundamental interest in chemical kinetics. In spite of many investigations, however, little is understood about the mechanism and the rate-controlling parameters.

Recently, Rebbert and Ausloos measured the efficiencies of various unsaturated hydrocarbons in quenching triplet acetone, and found that the efficiency of olefin depends strongly on its structure.[1] For quenching triplet benzene, Hanninger and Lee found that the efficiencies of ethylene derivatives depend greatly on the number of substitution; *i. e.*, the efficiency of tetramethylethylene is more than ten times as great as that of ethylene.[2] Similar results have been obtained by Morikawa and Cvetanović.[3] In the mercury-photosensitization, however, no such strong dependence has been observed.[4]

In this respect, the measurement of the efficiencies for quenching triplet cadmium atoms should be of interest because a triplet cadmium atom (Cd $5(^3P_1)$; 87.7 kcal) is similar to a triplet mercury atom (Hg $6(^3P_1)$; 112.7 kcal) in its electronic property and is close to triplet benzene (C_6H_6 $(^3B_{1u})$; 84.4 kcal[5]) in its excitation energy.

In cadmium-photosensitization, as was shown in a previous short communication,[6] the quenching efficiencies of ethylene derivatives are almost all the same and the trend of the efficiencies is similar to that obtained by quenching triplet mercury, but is different from those obtained by quenching triplet benzene and acetone. In the present paper, we will present the details of the measurement and of the date obtained after the previous communication was reported.

Experimental

Research-grade acetylene, ethylene, propylene, isobutene, 1-butene, *trans*- and *cis*-2-butenes, trimethylethylene, tetramethylethylene, cyclohexene, methyl-

1) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, **87**, 5569 (1965).

2) G. A. Hanninger, Jr., and E. K. C. Lee, *J. Phys. Chem.*, **71**, 3104 (1967).

3) A. Morikawa and R. J. Cvetanović, *Can. J. Chem.*, **46**, 1813 (1968).

4) R. J. Cvetanović, "Progress in Reaction Kinetics," Vol. 2, ed. by G. Porter, Pergamon Press, Oxford (1964), p. 67.

5) D. F. Evans, *J. Chem. Soc.*, **1959**, 2753.

6) S. Tsunashima and S. Sato, This Bulletin, **40**, 2987 (1967).

acetylene, vinylacetylene, 1,3-butadiene, propane, and cyclopropane supplied by the Takachiho Shoji Co. were used after bulb-to-bulb distillations. The gas-chromatographic analyses showed that the impurities were less than 0.5%. *Trans*- and *cis*-2-pentenes supplied by the Takachiho Shoji Co. were used after separating them from each other by gas chromatography. Hydrogen supplied by the Suzuki Shokan Co. was used after passing it through a trap at the temperature of liquid nitrogen. The mass-spectrometric analyses of acetylene-d_2 synthesized from calcium carbide and deuterium oxide, and ethylene-d_4 synthesized from deuterium and acetylene-d_2[7] showed that the isotopical impurities were less than 2%.

The light source and the apparatus were similar to those reported on in a previous paper.[8]

For each experiment, the pressure of *cis*-2-butene was kept almost constant (22—32 mmHg), while the pressure of the quencher was varied. After irradiation with a cadmium lamp at 270±1°C, the products were analyzed by gas chromatography using a column packed with dimethylsulforane on celite (30 m long) supplied by Shimadzu Co. Immediately after each run, the light intensity of the 3261 Å resonance line was measured using the cadmium-photosensitized *cis-trans* isomerization of *cis*-2-butene on the assumption of the quantum yield being 0.5.[8]

Treatment of the Data

The competitive quenching method used is based on the following reactions[8]:

$$\mathrm{Cd} + h\nu \longrightarrow \mathrm{Cd}^* \qquad (1)$$
$$\mathrm{Cd}^* + \mathrm{C} \longrightarrow \mathrm{Cd} + \mathrm{B}^* \qquad k_b \qquad (2)$$
$$\mathrm{Cd}^* + \mathrm{T} \longrightarrow \mathrm{Cd} + \mathrm{B}^* \qquad k_b \qquad (3)$$
$$\mathrm{Cd}^* + \mathrm{X} \longrightarrow \mathrm{Cd} + \mathrm{X}' \qquad k_x \qquad (4)$$
$$\mathrm{B}^* + \mathrm{M} \longrightarrow \tfrac{1}{2}\mathrm{C} + \tfrac{1}{2}\mathrm{T} + \mathrm{M} \qquad (5)$$

where Cd* and B* represent, respectively, a triplet cadmium atom and an excited 2-butene molecule which isomerizes to *cis*- or *trans*-2-butene after collisional deactivation. T and C are *trans*- and *cis*-2-butenes respectively. X is a quencher molecule. As has been suggested in a previous paper,[8] the spontaneous emission process of a triplet cadmium is negligible compared with the process of the isomerization at the higher-than-1 mmHg 2-butene.

The steady-state treatment of the above mechanism gives the following relation;

$$R_0/R = 1 + (k_x/k_b)([\mathrm{X}]/[\mathrm{B}]) \qquad (\mathrm{I})$$

where R_0 and R represent the rates of the isomerization of 2-butene in the absence and in the presence of quencher molecules respectively. k_x and k_b are the efficiencies of a quencher and 2-butene for quenching triplet cadmium atoms respectively.

Equation (I) suggests that the plots of R_0/R as a function of the concentration ratio, [X]/[B], should give a straight line and that the slope of the straight line is relative quenching efficiency of the quencher competitive with 2-butene, k_b/k_x. In the present study, *cis*-2-butene is used as the detector compound.

In order to achieve good analytical accuracy as regards the values of initial rate of the isomerization, it was necessary to make higher conversions. The initial rate of the isomerization was estimated from the raw data using Eq. (II). Equation (II) was derived under the assumptions that the quantum yield of the isomerization of 2-butene is 0.5 and that the efficiency of *trans*-2-butene in quenching triplet cadmium is equal to that of *cis*-2-butene.[8]

$$R = (([\mathrm{C}] + [\mathrm{T}])/2t) \ln (([\mathrm{C}] + [\mathrm{T}])/([\mathrm{C}] - [\mathrm{T}])) \qquad (\mathrm{II})$$

Here, t represents the reaction time. [C] and [T] are the amounts of *cis*- and *trans*-2-butenes respectively obtained after the irradiation.

Results and Discussion

Quenching Data. The presence of quencher molecules retarded the isomerization of 2-butene. The R_0/R ratio was plotted against the concentration ratio, [X]/[B]. Figure 1 shows typical

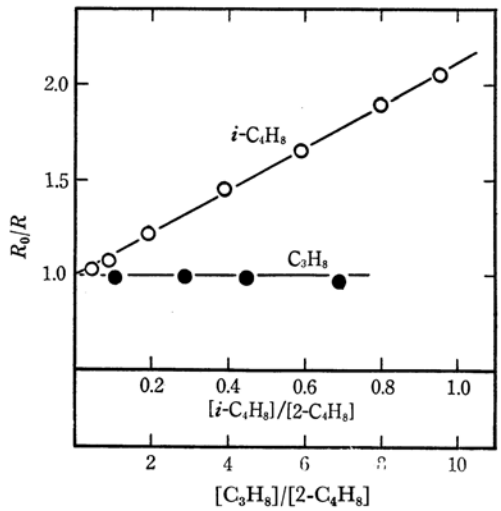

Fig. 1. The ratio of R_0/R as a function of the ratio of the pressure of competing quencher to that of *cis*-2-butene.

results obtained for propane and isobutene as competitive quenchers. Similar plots were obtained with all quenchers examined except for hydrogen. The case of hydrogen will be discussed later. The relative quenching efficiencies calculated from the slopes of the straight lines by the method of least squares are listed in Table 1. Table 1 also shows the relative quenching efficiencies for triplet cadmium,[9] mercury,[4] and

7) Y. Hatano, S. Shida and S. Sato, This Bulletin, **41**, 1120 (1968).

8) S. Tsunashima and S. Sato, *ibid.*, **41**, 284 (1968).

9) E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.*, **11**, 164 (1943).

TABLE 1. RELATIVE QUENCHING EFFICIENCIES

Quencher	$Cd(^3P_1)$		$Hg(^3P_1)$	Benzene		Acetone
	This work	a′	b′	c	d	e′
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
Isobutene	1.11 ± 0.03		0.95		1.27	0.66
cis-2-Butene	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)
cis-2-Pentene	1.03 ± 0.07					1.4
Trimethylethylene	1.02 ± 0.10			1.7 ± 0.2	1.61	1.4
Tetramethylethylene	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
Methylacetylene	1.24 ± 0.09					
Vinylacetylene	1.25 ± 0.02					
Cyclohexene	1.02 ± 0.07					0.90
Ethylene-d_4	0.96 ± 0.01					
Acetylene-d_2	0.94 ± 0.10					
Propane	0 ± 0.01	10^{-4}	0.045	~0		
Cyclopropane	0 ± 0.02	0.026	0.033			

a′ Ref. 9, b′ Ref. 4, c Ref. 2, d Ref. 3, e′ Ref. 1

acetone,[1] efficiencies which were determined by the physical method, and also for triplet benzene,[2,3] which were determined by the competitive quenching method. The relative efficiencies for quenching triplet cadmium measured by the present method agree with those obtained by the physical method within the range of experimental error.

Unsaturated Hydrocarbons. In the case of unsaturated hydrocarbons, the experimental accuracy can be expected to be very high, because unsaturated hydrocarbons strongly quench triplet cadmium and small amounts of impurities and/or small amounts of side-reaction products do not affect the main reactions. No measurable amounts of side-reaction products were observed in any case examined except in the cases of methylacetylene and *cis*-2-pentene. In the case of methylacetylene, allene was obtained even in a dark reaction at 270±1°C. In the case of *cis*-2-pentene, *trans*-2-pentene was formed with a high quantum efficiency. The quantum yield of *trans*-2-pentene increased with an increase in the concentration of *cis*-2-pentene (Fig. 2).

More serious systematic errors may arise from the neglect of the following reaction, if they occur:

$$X' + C(\text{or } T) \longrightarrow X + B^* \quad (6)$$
$$X' + M \longrightarrow X + M \quad (7)$$

where X′ represents an energized quencher molecule which is formed by the reaction (4). If the reaction (6) is involved in the mechanism, *i. e.*, if X′ can transfer its energy to 2-butene and cause the *cis-trans* isomerization, the slope of the straight line of the plots of R_0/R *vs.* [X]/[B] does not show the relative quenching efficiency. However, the reaction (6) may be neglected in the case of the quencher examined here, because: (a) the plots of R_0/R as a function of the concentration ratio showed a straight line in every case; (b) in the case of 2-pentene, the total quantum yield of the isomer formations of 2-butene and 2-pentene was 0.5 at various concentration ratios of 2-pentene to 2-butene (Fig. 2); (c) the value of the relative quenching efficiency of 2-pentene as estimated

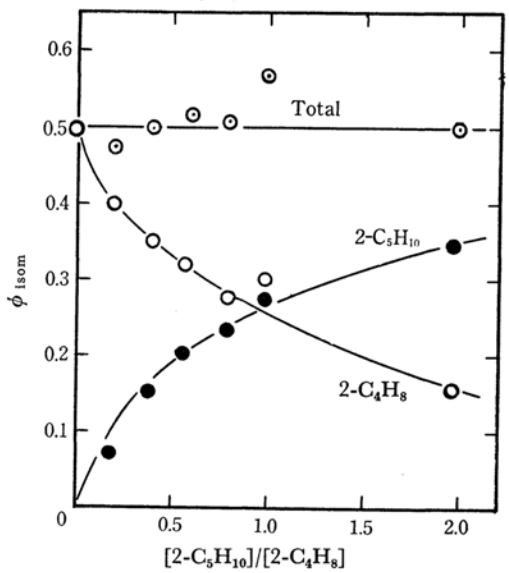

Fig. 2. Quantum yields of isomers formed in the reaction of the mixture of *cis*-2-butene and *cis*-2-pentene photosensitized by triplet cadmium at 270 ±1°C.

from the decrease in the rate of the isomerization of 2-butene is equal to that estimated from the increase in the rate of the isomerization of 2-pentene (Fig. 2); and (d) the quenching efficiencies determined by the present method agree well with those determined by the physical method* (Table 1).

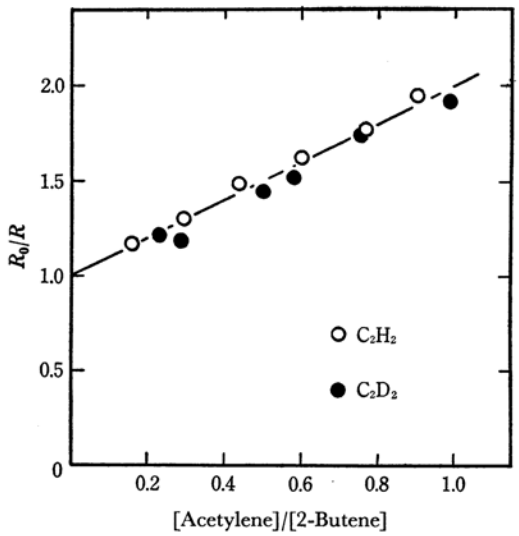

Fig. 3. Isotope effect in the quenching efficiency of acetylene for triplet cadmium atoms at 270±1°C.

Isotope Effects. As is shown in Fig. 3 and in Table 1 the isotope effect in quenching triplet cadmium atoms by acetylene or ethylene is negligibly small.

Comparison with Other Sensitizers. As is also shown in Table 1, the trend of quenching efficiencies obtained in the cadmium-photosensitization is similar to that obtained in the mercury-photosensitization and is different from those obtained in the benzene- and acetone-photosensitizations, in spite of the fact that the energy transferred in the cadmium-photosensitization is close to that transferred in the benzene-photosensitization.

The trend obtained in the acetone-photosensitization was explained by Rebbert and Ausloos as follows[1]: when the energy-transfer process is endothermic,*2 the quenching efficiency increases with a diminishment in the enthalpy change of the reaction. A similar consideration can explain the trend observed in the benzene-photosensitization, but not the trend in the cadmium-photosensitization, even though the quenching measurement of the cadmium-photosensitization were carried out at high temperatures (270±1°C). Morikawa and Cvetanović[3] found that the relative rates of the energy-transfer from the benzene triplet are affected by the temperature and that the apparent activation energy of the quenching efficiency of butadiene is about one kcal smaller than that of *cis*-2-butene. When the relative quenching efficiency of butadiene against *cis*-2-butene is extrapolated to 270°C using their data, it reduces to about 5. However, the relative quenching efficiency of butadiene in comparison with *cis*-2-butene in the cadmium-photosensitization is about unity. Although further experiments are needed, the difference in trend between benzene- and cadmium-photosensitizations is probably not due to the temperature.

Another possible explanation for the difference in the trend is the difference in the electronic property of the photosensitizer, as has been mentioned in a previous short communication.[6]

Saturated Hydrocarbons. The rate of the isomerization of *cis*-2-butene in the cadmium-photosensitization was scarcely affected at all by the addition of propane or cyclopropane. Non-condensible gases at the temperature of liquid nitrogen were not detected in the competitive quenching study. In the cadmium-photosensitized decomposition of pure propane, however, the formation of hydrogen was observed.[10] These results suggest that the quenching efficiency of saturated hydrocarbons is very low compared with that of olefins (Table 1). Therefore, in the reactions of pure saturated hydrocarbons, negligibly small amounts of impurities and side-reaction products may bring about a larger experimental error.

Table 2. Products from the reaction of the mixture of hydrogen and *cis*-2-butene photosensitized by triplet cadmium at 270±1°C[a]

Pressure of hydrogen mmHg	Products μmol				
	C_3H_6	C_4H_{10}	1-C_4H_8	*t*-C_4H_8[b]	*c*-C_4H_8[c]
0	0	0	0	4.70	30.4
8.92	0.60	0.50		4.41	28.5
11.9	0.74	0.57	0.11	4.16	27.6
16.6	0.90	0.77	0.22	4.20	27.9
21.2	1.10	0.82	0.19	3.95	26.7
26.8	1.21	0.97	0.22	3.91	27.6
31.7	1.32	1.13	0.26	3.95	25.5

a) Pressure of *cis*-2-butene: 25.1 mmHg
light intensity: 0.364 μE/min
irradiation time: 30 min
b) *trans*-2-butene
c) *cis*-2-butene

*1 The physical method is based on the measurement of the intensity of phosphorescence.[4]

*2 They compared the vertical triplet energies of olefins with the triplet energy of acetone. In the present authors' opinion, however, the lowest triplet energies of the olefins (which are twisted) should be used for the comparison. In this treatment, therefore, the energy transfer process will always be exothermic. However, their discussion of the trend is still relevant.

10) P. Agius and B. DeB Darwent, *J. Chem. Phys.*, **20**, 1679 (1952).

Hydrogen. As is shown in Table 2, propylene, *n*-butane, and 1-butene were formed together with *trans*-2-butene when a mixture of hydrogen and *cis*-2-butene was photosensitized by triplet cadmium. The quantum yields of the product formations increased with an increase in the pressure of hydrogen. The relative quenching efficiency of hydrogen could not be determined from Eq. (I) because of the large amounts of side-reaction products.

A possible reaction mechanism to account for the formations of propylene and *n*-butane is as follows:

$$Cd^* + C(\text{or } T) \longrightarrow Cd + B^* \qquad k_b \quad (2,3)$$

$$Cd^* + H_2 \rightarrow CdH + H \rightarrow Cd + 2H \qquad k_h \quad (8)$$

$$H + C_4H_8 \longrightarrow CH_3 + C_3H_6 \quad (9)$$

$$\longrightarrow C_4H_9 \quad (10)$$

$$2C_4H_9 \longrightarrow C_4H_8 + C_4H_{10} \quad (11)$$

$$\longrightarrow C_8H_{18} \quad (12)$$

where CdH formation is assumed following Bender and Olsen.[11] This compound, however, may decompose to cadmium and hydrogen atoms through collisions with other molecules, because the heat of the formation of CdH is estimated to be only 15.5 kcal.[10] Usually, the reaction (10) requires a collisional deactivation. Rabinovitch *et al.* found that the efficiency of 2-butene in deactivating the chemically-activated *s*-butyl radicals was much higher than that of hydrogen.[12] Therefore, the reaction (10) may be treated as pressure-independent under the present experimental conditions, *i. e.*, when the pressure of 2-butene is kept constant (25 mmHg) and when the pressure of hydrogen is varied (9—32 mmHg). The C_4H_8 formed by the reaction (11) involves 1-butene, *cis*-, and *trans*-2-butenes. This is the reason that the quenching efficiency of hydrogen can not be calculated with Eq. (I). In this experiment, the amounts of C_8-products formed by the reaction (12) have not been measured. This probably explains the material balance in Table 2.

The steady-state treatment of the above mechanism gives the following equations;

$$1/\phi(C_3H_6) = \tfrac{1}{2}(1+k_{10}/k_9)(1+(k_b/k_h)([B]/[H_2])) \quad (III)$$

$$1/\phi(C_4H_{10}) = (1+k_{12}/k_{11})(1+k_9/k_{10})(1+(k_b/k_h)([B]/[H_2])) \quad (IV)$$

where $\phi(C_3H_6)$ and $\phi(C_4H_{10})$ are the quantum yields of the propylene and *n*-butane formations respectively. k_h is the quenching efficiency of hydrogen, *i. e.*, the rate constant of the reaction (8). The relations of Eqs. (III) and (IV) are plotted in Fig. 4. The intercepts and the slopes of the straight lines in Fig. 4, as calculated by the method of least squares, are listed in Table 3. The

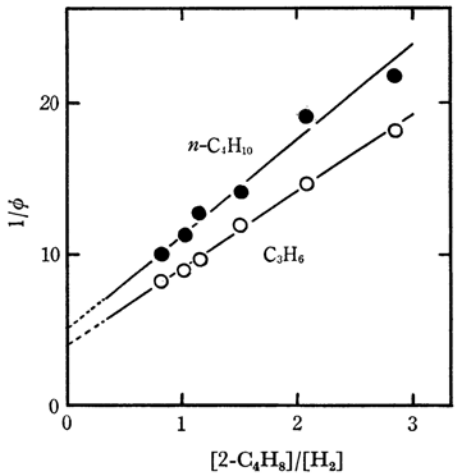

Fig. 4. Plots of the reciprocal of the quantum yields of propylene and *n*-butane formed in the reaction of hydrogen and *cis*-2-butene photosensitized by cadmium as a function of the concentration ratio of *cis*-2-butene to hydrogen.

TABLE 3. THE VALUES OF THE SLOPES AND THE INTERCEPTS OF THE STRAIGHT LINES IN Fig. 5

	Slope	Intercept	Slope/Intercept
$\phi(C_3H_6)$	5.1±0.2	4.0±0.3	1.3±0.1
$\phi(C_4H_{10})$	6.2±0.4	5.2±0.8	1.2±0.3

k_{12}/k_{11} value (the ratio of the disproportionation/recombination of *s*-butyl radicals) is estimated to be ~0.3. This value is appreciably lower than the value estimated by Kraus and Calvert (2.3),[13] but is close to that obtained by Rabinovitch *et al.* (~0.6).[12] The difference may be due to the difference in the source of the radical and/or to the neglect of other possible reactions of *s*-butyl radicals.

From the values of the intercepts and the slopes in Table 3, the relative quenching efficiency of hydrogen against *cis*-2-butene was calculated to be 0.83±0.18 (by using Eq. (IV)) and 0.79±0.08 (by using Eq. (III)). The agreement of these two values is satisfactory. Therefore, it can be said that the quenching efficiency of hydrogen is comparable to those of olefins.

11) P. Bender, *Phys. Rev.*, **36**, 1535 (1930), L. O. Olsen, *J. Chem. Phys.*, **6**, 307 (1938).

12) R. F. Kubin, B. S. Rabinovitch and R. E. Harrington, *J. Chem. Phys.*, **37**, 937 (1962), J. H. Current and B. S. Rabinovitch, *ibid.*, **41**, 2743 (1964).

13) J. W. Kraus and J. G. Calvert, *J. Am. Chem. Soc.*, **79**, 5921 (1957).