Comparison of the Direct and Sensitized Photolysis of 3-Methylpentanal in the Vapor Phase

R. E. Rebbert and P. Ausloos

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Abstract: The direct and the benzene- and acetone-sensitized photolysis of 3-methylpentanal produces butene-1, *trans*-butene-2, and *cis*-butene-2 by an intramolecular rearrangement process in which a hydrogen atom is transferred to the carbonyl group from a γ-carbon atom. In the direct photolysis an increase in temperature or a decrease in wavelength of the incident light results in an increase in the percentage yield of butene-1 and in the *cis*/*trans* ratio of butene-2. The distribution of the butenes depends upon the amount of energy given to the aldehyde whether by the direct or sensitized photolysis. The benzene- and acetone-sensitized experiments give additional evidence that the intramolecular rearrangement which involves the photoelimination of olefins can proceed through a triplet excited state. The following additional information was obtained in the course of this study: (1) the aldehyde undergoes both triplet–triplet and singlet–singlet energy transfer with benzene; (2) in the acetone–aldehyde systems only triplet–triplet energy transfer occurs; (3) a comparison of the distribution of butenes, which was obtained in the acetone-sensitized experiments with the butene distribution in the direct photolysis at the same temperature, indicates that <81 kcal are transferred to the aldehyde by acetone in a triplet–triplet energy-transfer reaction.

Previous investigations from this laboratory of the photolysis of *sec*-butyl acetate,[1,2] *sec*-butyl formate,[1] and 4-methylhexanone-2[2,3] have shown that three butene isomers are eliminated from each compound by an intramolecular rearrangement process in which a secondary or a primary hydrogen atom is transferred to the carbonyl group from a γ-carbon atom. In each case, the transfer of one of the three primary γ-hydrogen atoms resulted in the formation of butene-1 while the transfer of one of the two secondary γ-hydrogen atoms gave either *trans*- or *cis*-butene-2. Moreover, in the gas phase an increase of temperature of the system or a decrease in wavelength resulted in an increase in the percentage of butene-1 and in the *cis*/*trans* ratio of butene-2. The above studies have now been extended to include an aldehyde.

There is considerable evidence that for aldehydes and other carbonyl compounds the photoelimination of olefins in an intramolecular rearrangement process proceeds through a triplet excited state,[4] at least in the long-wavelength region of the absorption spectrum. For instance, 1-butanal quenches the phosphorescence of triplet acetone and the resulting excited 1-butanal molecule decomposed to form ethylene by an intramolecular rearrangement process with approximately the same quantum yield as was observed in the direct photolysis.[5] In corroboration of this, the addition of small quantities of biacetyl to 1-butanal quenched the formation of ethylene, and at the same time phosphorescence was observed from the triplet biacetyl while the quantum yield of the fluorescence emitted by the upper single state of the aldehyde remained constant.[6]

In view of the above observations, 3-methylpentanal was chosen as an appropriate compound for the further study of triplet–triplet energy transfer reactions. By comparing the distributions of the butenes from the direct photolysis at different wavelengths with the distributions produced by triplet–triplet energy-transfer processes at the same temperature, some information about the amount of energy transferred relative to the energy content of the triplet donor could be obtained. Benzene[7] and acetone[5,8] are known triplet donors and, therefore, they have been used to photosensitize the decomposition of 3-methylpentanal.

Experimental Section

Spectrograde acetone, benzene, and cyclohexane were obtained from the Distillation Products Industries. The 3-methylpentanal was synthesized by the Chemical Samples Co. and was purified on a spinning-band distillation column having the equivalent of 70 theoretical plates. All these compounds were thoroughly degassed before use and were stored at −80°.

The photolysis experiments were performed in a cylindrical quartz cell 10 cm long and 5 cm in diameter (185 cc in volume) which was connected to a conventional vacuum system through a metal valve. A Hanovia S-100 medium-pressure mercury arc was used as the light source in conjunction with a third-order Baird-Atomic 2537-A interference filter. For the 3340-A experiments, an Osram 200 high-pressure mercury arc was used with a Corning 7-37 filter which eliminates the 3130-A line. The same lamp was used with a third-order Baird-Atomic 3130-A interference filter for experiments at 3130 A.

After photolysis, the noncondensable gases were distilled from the reaction mixture at −195° through a Toepler pump, measured in a gas buret, and analyzed on a mass spectrometer. The other products were distilled at approximately −100° and analyzed on a gas chromatograph equipped with a flame ionization detector.

Quantum yields are based on the rate of production of carbon monoxide in the photolysis of pure acetone at 150°. At this temperature and at the intensities used in this study ($I_a = 3 \times 10^{11}$ quanta/cc-sec at 2537 A and 6×10^{13} quanta/cc-sec at 3130 A) the quantum yield of carbon monoxide may be taken as unity.[9]

The emission measurements were conducted in a high-quality quartz fluorescent T-shaped cell, 56 mm long and 28 mm in diameter. The gases were continuously circulated through the cell

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[1] R. Borkowski and P. Ausloos, *J. Am. Chem. Soc.*, **83**, 1053 (1961).

[2] R. E. Rebbert and P. Ausloos, *J. Chem. Phys.*, 37, 1158 (1962).

[3] P. Ausloos, *J. Phys. Chem.*, **65**, 1616 (1961).

[4] P. Ausloos and R. E. Rebbert, *J. Am. Chem. Soc.*, **86**, 4512 (1964).

[5] R. E. Rebbert and P. Ausloos, *ibid.*, **86**, 4803 (1964).

[6] R. P. Borkowski and P. Ausloos, *ibid.*, **84**, 4044 (1962).

[7] R. B. Cundall, F. J. Fletcher, and P. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964).

[8] R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, 87, 1847 (1965); G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

[9] P. S. Herr and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **62**, 2052 (1940).

Table I. Photolysis of 3-Methylpentanal at 3340 A in the Vapor Phase

Temp, °C	Pressure of aldehyde, torr	$R_{C_4H_8}$,[a] cc/min × 10^4	Distribution of butenes, % Butene-1	*trans*-Butene-2	*cis*-Butene-2	Butene-2 ratio *cis*/*trans*
28	14		5.5	73.0	21.5	0.30
51	14	2.84	6.1	71.5	22.4	0.31
96	14		7.1	69.7	23.2	0.33
154	18	3.00	9.1	67.8	23.2	0.34
200	20	3.27	11.1	65.4	23.5	0.36
248	21	3.32	11.2	65.4	23.4	0.36
302	21.5	8.86	28.6	51.2	20.2	0.40

[a] These experiments were performed at constant incident intensity so that the rate of butene formation is proportional to the quantum yield.

Table II. Photolysis of 3-Methylpentanal at 3130 and 2537 A in the Vapor Phase

Temp, °C	Pressure of aldehyde, torr	$\Phi_{C_4H_8}$	Distribution of butenes, % Butene-1	*trans*-Butene-2	*cis*-Butene-2	Butene-2 ratio *cis*/*trans*
			3130 A			
26	14[a]		10.3	68.0	21.7	0.32
27	14	0.34	10.1	67.5	22.4	0.33
50	14	0.30	9.8	68.0	22.2	0.33
151	18	0.34	12.8	64.1	23.1	0.36
151	1.8		13.8	61.8	24.4	0.40
245	21	0.67	18.1	57.2	24.7	0.43
			2537 A			
28	14	0.58	18.1	56.9	25.0	0.44
53	14	0.70	19.4	56.1	24.5	0.44
150	17	0.67	20.7	54.0	25.2	0.47
207	19.5	0.73	22.2	53.0	24.8	0.47
257	14	1.2	27.3	48.8	23.9	0.49

[a] 82 torr of cyclohexane added.

with an all-glass pump. The light emitted by the gas at right angles to the exciting beam passed through a quartz window and a filter to a 1 P28 photomultiplier tube. The light emitted by the acetone–aldehyde mixtures and by the benzene–aldehyde mixtures passed through a Corning 0-51 and 7-54 filter, respectively. The former filter transmitted wavelengths above 3500 A and the latter, in the range from 2300 to 4200 A. A Bausch & Lomb high-intensity grating monochromator with a dispersion of 3.2 mμ/mm and an exit slit of 3.0 mm was used in conjunction with a Hanovia S-100 mercury lamp as the light source.

Results

Direct Photolysis of 3-Methylpentanal. The distributions of the butenes formed in the direct photolysis of 3-methylpentanal in the vapor phase at various temperatures and wavelengths are given in Tables I and II. It is to be noted (Table II) that a tenfold change in pressure or the addition of 83 torr of cyclohexane has only a minor effect on the distribution of butenes formed at 3130 A. In addition to the results shown in the tables, it was also noted that a sixfold change in conversion at 52° and 3340 A had essentially no effect on the butene distributions. In addition, below 200° the addition of radical scavengers such as oxygen or nitric oxide at a concentration of about 10% did not appreciably affect the distribution or quantum yields of product butenes.

Fluorescence and Phosphorescence. No phosphorescent emission above 3500 A from 3-methylpentanal was observed at the incident wavelengths used in this investigation. However, with 3130-A incident light, there was a small amount of fluorescence from the aldehyde which was unaffected by the addition of 3.6 torr of oxygen. This emission was about one-third the intensity of fluorescence expected from a similar concentration of acetone at the same wavelength. At 3340 A the fluorescent intensity from the aldehyde was down by a factor of 3 or 4, and at 2537 A there was no emission within experimental error. Photolysis of benzene–3-methylpentanal (1:0.1 or 1:1) mixtures at 2537 A did not result in any benzene-sensitized emission from the aldehyde, although the aldehyde did quench the fluorescent emission of the benzene. As shown in Figure 1, a plot of Q_0/Q *vs.* the pressure of aldehyde yields a straight line up to about 2 torr of aldehyde. Q is the fluorescent emission from benzene in the presence of 3-methylpentanal. Q_0 is the emission from pure benzene measured at the same incident intensity.

The phosphorescence of acetone is also quenched by the addition of 3-methylpentanal as seen in Figure 1 where $(Q_T)_0/Q_T$ is plotted against the aldehyde pressure. Q_T was obtained by substracting the constant emission observed in the acetone–aldehyde mixtures in the presence of oxygen from the total emission observed in the absence of oxygen. $(Q_T)_0$ is the emission calculated in the same way but for pure acetone. The relative intensity of emission from acetone in the presence of oxygen is unaffected by the addition of 3-methylpentanal, indicating that the aldehyde has no affect on the fluorescent emission from acetone (see Figure 2).

Benzene- and Acetone-Sensitized Decomposition of 3-Methylpentanal. Table III shows the results for the benzene-sensitized photolysis of 3-methylpentanal at 2537 A and at 27 and 151°. Figure 3 shows a plot of the ratio butene-1/butene-2 (right-side ordinate) and of the decrease in fluorescence of benzene (left-side ordinate) *vs.* aldehyde pressure at 27° and 2537 A. The two curves are very similar in appearance.

The results for the acetone-sensitized decomposition of the aldehyde are given in Table IV. Figure 4 shows

Table III. Benezene-Sensitized Photolysis of 3-Methylpentanal at 2537 A

Pressure of aldehyde, torr	$\Phi_{C_4H_8}$	Distribution of butenes, % Butene-1	*trans*-Butene-2	*cis*-Butene-2	Butene-2 ratio *cis*/*trans*
		27°[a]			
0.02	0.09	5.2	72.6	22.3	0.31
0.04	0.12	5.5	72.1	22.4	0.31
0.1	0.15	6.1	71.3	22.6	0.32
0.2	0.15	6.4	70.8	22.7	0.32
0.6	0.16	7.9	69.3	22.8	0.33
1.1	0.16	8.4	68.8	22.8	0.33
1.1[b]	0.14	6.3	72.0	21.7	0.30
2.5	0.15	9.8	67.3	23.0	0.34
6.1	0.15	10.6	66.3	23.1	0.35
12.2	0.14	12.4	63.8	23.8	0.37
		151°[c]			
0.03	0.02	7.4	67.6	25.0	0.37
0.15	0.04	7.7	66.9	25.4	0.38
0.45	0.05	8.1	66.9	25.0	0.37
0.45[d]	0.06	8.0	67.2	24.7	0.37
1.1	0.07	9.9	65.9	24.2	0.37
5.7	0.09	10.2	65.1	24.8	0.38

[a] Pressure of benzene, 80 torr. [b] 80 torr of cyclohexane added. [c] Pressure of benzene, 113 torr. [d] 113 torr of cyclohexane added.

a plot of the quantum yield of butene formation (right-side ordinate) and of the decrease in phosphorescence of acetone (left-side ordinate) *vs.* the pressure of aldehyde. These two curves also follow similar trends.

Table IV. Acetone-Sensitized Photolysis of 3-Methylpentanal[a]

Pressure of aldehyde, torr	$\Phi_{C_4H_8}$	Distribution of butenes, % Butene-1	*trans*-Butene-2	*cis*-Butene-2	Butene-2 ratio *cis*/*trans*
		3130 A, 27°			
0.2	0.12	4.8	74.2	21.0	0.28
0.5	0.20	4.6	74.6	20.8	0.28
1.1	0.22	4.5	75.0	20.5	0.27
2.6	0.27	4.5	75.0	20.5	0.27
2.7[b]	...	4.8	74.7	20.5	0.27
6.2	0.30	4.6	74.7	20.7	0.28
		148°			
0.6	0.007	9.1	67.1	23.8	0.36
1.0	0.01	9.0	66.3	24.8	0.37
3.0[b]	...	9.9	66.9	23.2	0.35
3.0	0.02	9.1	66.7	24.2	0.36
6.0	0.04	9.2	67.1	23.7	0.35
14.0	0.05	9.2	66.8	24.0	0.36
		2537 A, 27°			
0.8	...	5.6	73.4	21.0	0.29
6.0	...	5.6	73.5	20.9	0.28

[a] Concentration of acetone, 8.0×10^{-3} *M* (this concentration corresponds to 150 torr at 27°). [b] Neutral density filter reduced the intensity about 15-fold.

Direct photolysis of the aldehyde in these sensitized experiments can be neglected in view of the high extinction coefficient of benzene compared to the aldehyde at 2537 A and the relatively low pressures of aldehyde that were used in most experiments.

Discussion

Direct Photolysis of 3-Methylpentanal. Earlier studies[10] of the photolysis of aliphatic aldehydes having hydrogen atoms in the γ position from the carbonyl group have shown that the following three primary processes may be expected to occur in the direct photolysis of 3-methylpentanal in the region 2537–3340 A.

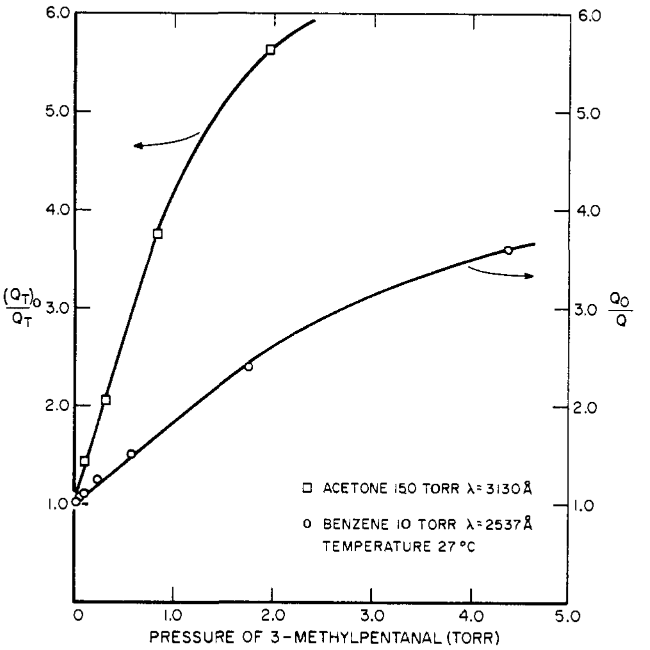

Figure 1. Right-side ordinate: ○, Q_0/Q for benzene at 2537 A and 27° *vs.* pressure of aldehyde. Left-side ordinate: □, $(Q_T)_0/Q_T$ for acetone at 3130 A and 27° *vs.* pressure of aldehyde.

$$CH_3CH_2CH(CH_3)CH_2CHO + h\nu \longrightarrow C_5H_{11} + CHO \qquad (I)$$

$$\longrightarrow C_4H_8 + CH_3CHO \qquad (II)$$

$$\longrightarrow C_5H_{12} + CO \qquad (III)$$

Process II may proceed by any one of three paths. The transfer of a primary γ hydrogen to the carbonyl group leads to the formation of butene-1, while the transfer of a secondary γ hydrogen gives either *cis*- or *trans*-butene-2. Below 200°, the product butene can be entirely attributed to an intramolecular rearrangement process such as II, as is evidenced by the facts that (1) the quantum yield of butene is constant with an increase in temperature from 25 to 200° and (2) below 200°, the addition of 10% oxygen (see Results) does not change the quantum yield or the distribution of the butenes. At temperatures above 200°, the increase in the butene quantum yield and the drastic increase in the relative amount of the butene-1 isomer formed seem to indicate that a thermal reaction is contributing to the formation of butene-1. This can be accounted for by the decomposition of the isopentyl radical formed in process I at the higher temperatures.

$$CH_3CH_2CH(CH_3)CH_2 \longrightarrow CH_3CH_2CH{=}CH_2 + CH_3$$

Below 200°, where the pyrolysis of the isopentyl radical is unimportant, it is seen (Tables I–III) that the relative importance of the transfer of a primary γ hydrogen in process II to form butene-1 increases with increasing energy or temperature, while the formation of *cis*-butene-2 increases relative to that of *trans*-butene-2. Because secondary carbon–hydrogen bonds are weaker than primary bonds, the formation of butene-1 by process II does indeed require a greater amount of energy. In addition, *trans*-butene-2 is thermody-

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(10) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, Chapter 5.

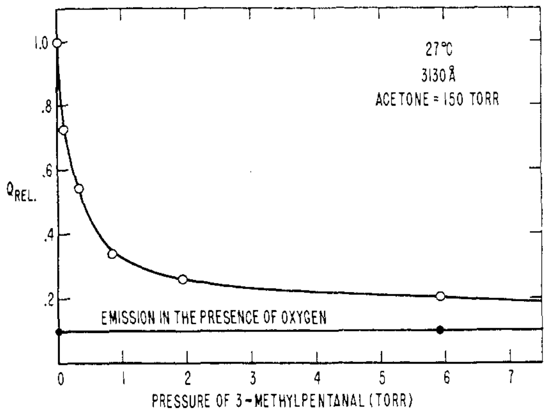

Figure 2. The relative emission, Q_{Rel}, from acetone *vs.* pressure of aldehyde at 3130 A and 27°: ●, 2 torr of oxgyen added.

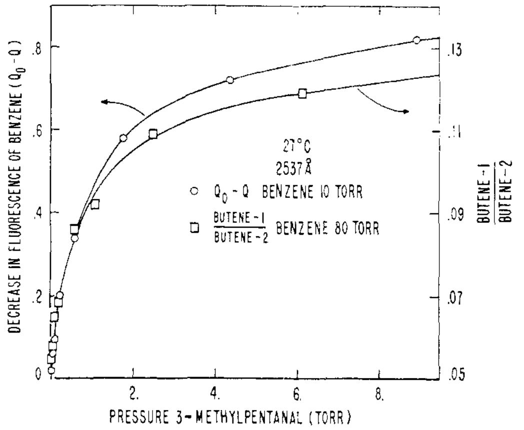

Figure 3. Right-side ordinate: □, ratio of butene-1/butene-2 from the benzene-sensitized photolysis at 2537 A and 27° *vs.* pressure of aldehyde. Left-side ordinate: O, the decrease in the fluorescence of benzene, $Q_0 - Q$, at 2537 A and 27° *vs.* pressure of aldehyde.

namically more stable than *cis*-butene-2 by about 1 kcal.[11]

Since intramolecular rearrangement processes exactly analogous to II occur in the photolysis of *sec*-butyl acetate, *sec*-butyl formate, and 4-methylhexanone-2, it is of interest to compare the butene distributions formed in these systems with those observed in this investigation. The same trends with energy and temperature changes are observed in all systems. Table V shows a direct comparison of analogous experimental results for 3-methylpentanal and for 4-methylhexanone-2. For the ketone, the intramolecular rearrangement process leading to butene formation is

$$CH_3COCH_2CH(CH_3)CH_2CH_3 + h\nu \longrightarrow CH_3COCH_3 + C_4H_8 \quad (IV)$$

The results given in Table V show that under similar conditions the distributions of the butenes formed in the 3-methylpentanal photolysis are nearly identical with those observed in the 4-methylhexanone-2 system. This is somewhat surprising since one would expect that under otherwise identical conditions a larger fraction of the excess energy would be removed by the butenes produced in the photolysis of the aldehyde in view of the smaller number of vibrational modes in the acetaldehyde product of process II compared to the acetone product of process IV. In the comparison of the distributions produced in the photolysis of *sec*-butyl acetate and *sec*-butyl formate[1] in which the intramolecular rearrangement process may be represented as

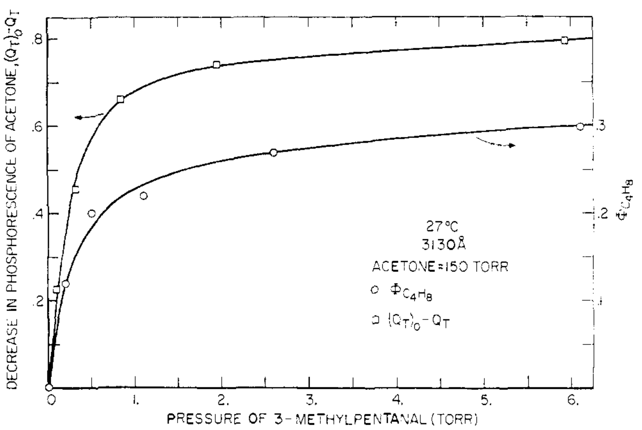

Figure 4. Right-side ordinate: O, quantum yield of butene formation for the acetone-sensitized photolysis at 3130 A and 27° *vs.* the pressure of aldehyde. Left-side ordinate: □, the decrease in phosphorescence of acetone, $(Q_T)_0 - Q_T$, at 3130 A and 27° *vs.* pressure of aldehyde.

$$CH_3COOCH(CH_3)CH_2CH_3 + h\nu \longrightarrow C_4H_8 + CH_3COOH$$
$$HCOOCH(CH_3)CH_2CH_3 + h\nu \longrightarrow C_4H_8 + HCOOH$$

the observed percentage of butene-1 and the *cis/trans* ratio of butene-2 was higher for the formate than the acetate under similar conditions. The lack of any appreciable difference in the butene distributions from the ketone and aldehyde may be due to the smaller percentage increase in the number of degrees of freedom in going from acetaldehyde to acetone (60%) in comparison with the increase in going from formic acid to acetic acid (100%). In addition, it must also be remembered that the incident light used for comparing the two esters was of a shorter wavelength (<2300 A) than that used for comparing the ketone and aldehyde. This means that there was a larger amount of excess energy to be distributed to the various fragments in the case of the esters. Thus, a small difference in the percentage of the excess energy which goes to the butene fragments would involve a larger absolute difference in energy for the esters in comparison to the ketone and aldehyde.

Sensitized Photolysis of 3-Methylpentanal. The change in the butene distribution with wavelength and the relative insensitivity of this distribution with pressure indicate that in a sensitized reaction a measurement of the relative yield of the three butene isomers may be used as an indication of the amount of energy transferred to the aldehyde by this energy-exchange process. Benzene and acetone have been used to photosensitize the decomposition of 3-methylpentanal.

In the benzene-sensitized system at 2537 A, the following reactions can account for most observations.

$$B + h\nu \longrightarrow B^1$$
$$B^1 (+ M) \longrightarrow B^3 (+ M) \quad (1)$$
$$B^1 \longrightarrow B + h\nu_F \quad (2)$$
$$B^3 + A \longrightarrow B + A^3 \quad (3)$$

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[11] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

Table V. Comparison of the Butene Distribution from the Photolysis of 3-Methylpentanal and 4-Methylhexanone-2[3]

	λ, A	Temp, °C	Pressure, torr	Butene distribution, % Butene-1	*trans*-Butene-2	*cis*-Butene-2	Butene-2 ratio *cis*/*trans*
Ketone	3130	44	7	9.7	68.5	21.8	0.32
Aldehyde	3130	50	14	9.8	68.0	22.2	0.33
Ketone	3130	150	7	13.0	64.3	22.7	0.35
Aldehyde	3130	151	14	12.8	64.1	23.1	0.36
Ketone	2537	44	7	21.3	55.2	23.5	0.40
Aldehyde	2537	53	14	19.4	56.1	24.5	0.44

$$B^1 + A \longrightarrow B + A^1 \qquad (4)$$

$$A^1 (+ M) \longrightarrow A^3 (+ M) \qquad (5)$$

$$A^3 \longrightarrow C_4H_8 + CH_3CHO \qquad (6)$$

B^1 and B^3 represent the first excited singlet and triplet states of benzene, respectively, and A^1 and A^3 represent the first excited singlet and triplet states of 3-methylpentanal.

The energy associated with the $^3B_{1u}$–$^1A_{1g}$ transition in benzene is about 84 kcal (3400 A).[12] Although benzene does not phosphoresce in the gas phase, Ishikawa and Noyes[13] have shown the existence of a triplet excited benzene by using biacetyl as a triplet acceptor. Now if the energy difference between the ground singlet and first excited triplet states of 3-methylpentanal is less than that for benzene, then benzene should act as a donor in a triplet–triplet energy-transfer reaction with the aldehyde as in reaction 3. Furthermore, the distribution of the butenes produced should be just slightly different than that in the direct photolysis at 3340 A and the same temperature. The results presented in Table III show that the distribution of the butenes at very low aldehyde concentrations is approximately what was expected for a triplet–triplet energy transfer from benzene at either 27 or 151°. However, as the concentration of aldehyde increases the distribution of butenes also continues to change. These results may be explained if, at high pressures of 3-methylpentanal, the aldehyde also quenches the singlet excited state of benzene as shown in reaction 4. A similar situation was observed for the benzene–biacetyl system in which both singlet and triplet excited benzene were quenched at sufficiently high concentrations of biacetyl.[13] The first excited singlet state of benzene is about 109 kcal above the ground state, and, consequently, if the butenes are only formed by a singlet–singlet energy transfer between benzene and the aldehyde, then the distribution should correspond to that for the direct photolysis at ~2600 A. Since benzene does fluoresce from its first excited singlet state (reaction 2), the quenching effect of 3-methylpentanal on singlet benzene was determined by measuring this emission from benzene with added aldehyde. The results which are given in Figures 1 and 3 show that 3-methylpentanal does indeed quench the fluorescence of benzene. This fact coupled with the change in butene distribution at increasing aldehyde pressures strongly indicates that besides a triplet–triplet energy transfer from benzene to the aldehyde (reaction 3) there is also a singlet–singlet transfer (reaction 4). Moreover, the similarity in the curves, given in Figure 3, for the decrease in fluorescence of benzene (left-side ordinate) and the increase in the ratio of butene-1/butene-2 (right-side ordinate) *vs.* aldehyde pressure gives further evidence that the change in the butene distributions is directly related to the decrease in benzene fluorescence, that is, that the decrease in fluorescence is a result of a singlet–singlet energy transfer from benzene to 3-methylpentanal. The distribution of the butenes produced in this sensitized photolysis will be a composite of that expected for the two different transfers. At high pressures of aldehyde (above 12 torr) there will be relatively more singlet–singlet transfer. It is only at very low pressures of aldehyde (below 0.1 torr) where triplet–triplet transfer predominates that the distribution of butenes is as expected for approximately 84 kcal of energy transferred.

The fact that the quantum yield of butene formation reaches a plateau at pressures greater than 0.1 torr of aldehyde indicates that all triplet excited benzene molecules are quenched by the aldehyde at this pressure. However, the experiments on the quenching of benzene fluorescence by the aldehyde and the change in the butene distribution indicate that at higher concentrations of aldehydes, singlet excited benzene molecules are quenched by the aldehyde. Apparently for each butene molecule formed from a singlet–singlet transfer there is, within experimental error, one less from a triplet–triplet energy transfer to the aldehyde. At 151° the shorter lifetime of the triplet benzene results in a lower quantum yield of butene, and a much higher pressure of aldehyde is needed before a plateau is reached. The addition of 80 torr of cyclohexane to the benzene–aldehyde mixtures at 27° does not appreciably change the quantum yield of butene formation, but it does change the distribution of the butenes. This change can be explained if cyclohexane either deactivates the excited single benzene or induces a singlet–triplet transition in benzene. Deactivation of the excited singlet to the ground state should result in a decrease in the butene quantum yield. The results are not accurate enough to say whether or not there is a small decrease in the quantum yield of butene. However, Ishikawa and Noyes[13] give results which show that cyclohexane quenches the fluorescence of benzene to a slight extent. At 151° neither the quantum yield of the formation of the butenes nor their distribution change with the addition of 113 torr of cyclohexane. This is not too surprising in view of the fact that, at the low pressure of aldehyde used (0.45 torr), the butene distribution has not changed very much from what was expected for just a triplet–triplet energy transfer from benzene at 151°. For instance, compare this butene distribution with that obtained for the direct photolysis at 3340 A and 151°. Thus, the contribution of any

(12) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

(13) H. Ishikawa and W. A. Noyes, Jr., *J. Chem. Phys.*, 37, 583 (1962).

singlet–singlet transfer to the formation of butene is still very small at this low pressure of aldehyde.

Some idea of the fraction of the absorbing benzene molecules which undergo an intersystem crossover to the triplet state may be obtained by comparing the maximum quantum yield of butene formation at high aldehyde pressure (>0.1 torr) in the benzene-sensitized photolysis (0.16) at 27° with the quantum yield measured in the direct photolysis. In the region of high aldehyde concentration, all triplet excited benzene molecules should transfer their energy to the aldehyde. Although at these high pressures of aldehyde we are deactivating a few singlets as well as triplets, it must be remembered that within experimental error for each butene formed from a singlet–singlet transfer there is approximately one less from a triplet–triplet transfer. Now if every triplet excited aldehyde molecule decomposed into a butene, then the quantum yield of benzene-sensitized butene formation in the plateau region would give the fraction of benzene molecules in the triplet state. Since other processes must occur for the excited aldehyde, it is necessary to know what fraction of the excited aldehyde molecules give butene. Apparently, this fraction changes with wavelength (0.34 at 3130 A and 0.58 at 2537 A). Thus, the comparison of the butene quantum yields for the benzene-sensitized photolysis should be made with the direct photolysis at 3400 A, since this wavelength corresponds approximately to the triplet-state energy transferred by benzene to the aldehyde. The quantum yield for the direct photolysis at 3400 A is probably not much less than at 3130 A. This follows because, as we shall see later, the acetone-sensitized photolysis of the aldehyde corresponds to the direct photolysis at approximately 3500 A, and the maximum quantum yield for butene formation obtained from this acetone-sensitized photolysis is 0.30. Moreover, in the photolysis of acetone at 3130 A, the yield of products is predominately from the first excited triplet state.[14] Consequently, this comparison of the quantum yield of butene formation from the benzene-sensitized photolysis with that expected for the direct photolysis at approximately 3400 A indicates that about 50% of the absorbing benzene molecules undergo an intersystem crossover to the triplet. This is to be compared with the value of 63% obtained by Cundall, Fletcher, and Milne[15] and more recently by Noyes, Mulac, and Harter.[16]

Acetone is another compound which has both a triplet and a singlet excited state, and in addition it exhibits both phosphorescence from the triplet state and fluorescence from the singlet state. The following simplified mechanisms can be used to account for most observations in the acetone-sensitized photolysis.

$$\mathrm{K} + h\nu \longrightarrow \mathrm{K}^1$$

$$\mathrm{K}^1 \longrightarrow \mathrm{K}^3 \tag{7}$$

$$\mathrm{K}^1 \longrightarrow \mathrm{K} + h\nu_\mathrm{F} \tag{8}$$

$$\mathrm{K}^3 \longrightarrow \mathrm{K} + h\nu_\mathrm{P} \tag{9}$$

$$\mathrm{K}^3 \longrightarrow \text{products} \tag{10}$$

$$\mathrm{K}^3 + \mathrm{A} \longrightarrow \mathrm{K} + \mathrm{A}^3 \tag{11}$$

$$\mathrm{A}^3 \longrightarrow \mathrm{C_4H_8} + \mathrm{CH_3CHO} \tag{6}$$

K^1 and K^3 represent the first excited singlet and triplet states of acetone. The energy difference for the 0–0 band of the triplet–singlet transition (reaction 9) in acetone is not known, but according to Hammond, *et al.*,[17] it is more than 70 kcal (<4000 A). At 3130 A and 25° the yield of products from the singlet state of acetone is a small fraction of the total primary quantum yield.[14] Moreover, it has been shown previously[3] that aldehydes in general quench only the triplet excited state of acetone. They do not affect this singlet excited state. That this is also true for 3-methylpentanal is seen in Figure 2. Here we notice that in the presence of oxygen the fluorescent light emitted by acetone is independent of the amount of aldehyde added while the phosphorescent light continues to decrease with an increase in aldehyde pressure. Thus the aldehyde quenches only the phosphorescence emitted by acetone. It does not affect the fluorescence of acetone. This means that in the case of the acetone-sensitized photolysis, unlike the case of the benzene-sensitized reaction, the distribution of the butenes should not change with an increase in aldehyde concentration. Table IV shows that the distribution of butenes is indeed independent of the aldehyde concentration at both 27 and 148°. Even a change in wavelength from 3130 to 2537 A has only a minor effect on this distribution. This means that triplet–triplet energy transfer from acetone to the aldehyde (reaction 11) is occurring from approximately the same low-lying vibrational energy level independent of the energy of the incident light. The comparison of the butene distribution which was obtained at 3130 A and 27° by the acetone-sensitized photolysis with that obtained in the direct photolysis of the aldehyde at the same temperature indicates that about 81 kcal (~3500 A) of energy was transferred from the triplet excited acetone to 3-methylpentanal. This is a maximum value, since it is based on the assumption that in the direct photolysis of the aldehyde there is an intersystem crossing from the excited singlet to the triplet state without the appreciable loss of vibrational energy. Any such loss of energy would lead to a lower value for this energy transfer and, consequently, for the energy difference for the triplet–singlet transition in acetone.

It is interesting to compare this quenching of the phosphorescence of acetone by 3-methylpentanal with the other aldehydes reported previously.[3] The slope of the straight-line portion of the curve given in Figure 1 (left-side ordinate) is a measure of the relative quenching rate, k_q, of 3-methylpentanal on the phosphorescence of acetone. This relative quenching rate (see Table VI) follows the same trend as that exhibited earlier by other aldehydes on the phosphorescence of acetone; that is, k_q increases with the chain length. The curvature which is seen in this plot at aldehyde pressures above 1 torr was also observed for all the other saturated aldehydes. A few other compounds are included in Table VI for comparison purposes.

With an increase in temperature, the butene distribution from the acetone-sensitized photolysis of

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[15] R. B. Cundall, F. J. Fletcher, and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964).

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Table VI. The Relative Quenching of Phosphorescence of Acetone by Various Additives

Compound	k_q	Compound	k_q
Ethanal	0.95	Oxygen	140
Propanal	1.9	Nitric oxide	380
1-Butanal	2.7	Sulfur dioxide	500
3-Methylpentanal	5.9	Styrene	4800
2-Butenal	100[a]		

[a] 2-Butenal is arbitrarily taken as 100.

3-methylpentanal changes as expected. Similar changes occurred in the direct and benzene-sensitized photolysis. However, at 148° the distribution of the butenes from the acetone-sensitized photolysis corresponds to the direct photolysis at 3340 A. This is in contrast to the results of the acetone-sensitized experiments at 27° in which the distribution corresponds to the direct photolysis at ~3500 A. This difference in results at the two temperatures may be caused by secondary reactions since a greater number of free radicals are present at the higher temperature in the photolysis of acetone. In agreement with this it is to be noted that a 15-fold reduction in intensity causes a change in the butene distribution at 148°, while it has essentially no effect at 27°. Likewise, the results for the benzene-sensitized photolysis at 27 and 151°, at which temperatures the concentration of free radicals must be very low, are consistent with a triplet–triplet energy transfer of 84 kcal at both temperatures.

The similarity in the curves (Figure 4) for the decrease in the phosphorescence of acetone (left-side ordinate) and the increase in the quantum yield of the butene (right-side ordinate) *vs.* aldehyde pressure gives further evidence that a triplet–triplet energy-transfer reaction produces the butene in the acetone-sensitized photolysis. Finally, it must be emphasized that, although the results give further evidence that the intramolecular rearrangement reaction proceeds through a triplet excited state, irrespective of the nature of the excited state, the butene distribution depends only on the amount of energy given to the aldehyde whether by the direct or by the sensitized photolysis.

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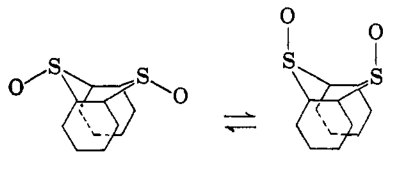
Evidence for an Inversion Degree of Freedom of *cis*-5,10-Thianthrene Dioxide

K. F. Purcell and J. R. Berschied, Jr.

Contribution from the Department of Chemistry, Wake Forest College, Winston-Salem, North Carolina. *Received October 3, 1966*

Abstract: A study of the temperature dependence of the proton resonance of *cis*-5,10-thianthrene dioxide in 1,1,2,2-tetrachloroethane and chloroform has shown the occurrence of an inversion degree of freedom for this molecule. The solvent chloroform appears to appreciably hydrogen bond to the phenyl π electrons. The inversion rate may be placed at greater than 100 sec^{-1}.

Thianthrene and its oxides have been studied by ultraviolet,[1] infrared,[2] and polarizability[3] techniques, and the radical cations and anions have been examined by electron spin resonance.[4,5] In addition, the crystal structures[6] of most members of this class of compounds have also been determined. Some of these studies[2,3] have led to conflicting conclusions regarding the occurrence of a "flapping" or inversion degree of freedom for the *cis*-5,10-thianthrene dioxide.



In the crystal the dihedral angle of the *anti* isomer has been found[6d] to be 123°. Polarizability studies[3] in benzene suggest that a rapid inversion occurs in solution, while solvent-effect studies[2] by infrared were interpreted as negative evidence for the occurrence of inversion at room temperature. There seems to be no obvious reason to expect a lack of inversion for this molecule. On the contrary, molecular models show that inversion is possible with very little strain on the σ framework; neither does it seem likely that C–S π bonding could create a high barrier to inversion. In fact, approximate molecular orbital calculations[7] for thianthrene place the energy of activation for inversion at only ~6 kcal/mole, and an SCF calculation[8] for thiophene indicates very little C–S π bonding.

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