

## ON THE ROLE OF NAPHTHALENE IN TYPE II PHOTOCLEAVAGE OF 4-METHYLPENTAN-2-ONE IN SOLUTION

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(Received October 8, 1979)

### Summary

The type II photocleavage of 4-methylpentan-2-one ( $c = 0.1 \text{ mol dm}^{-3}$ ) in *n*-heptane solution at 20 °C in the presence of naphthalene ( $c = 0.02 - 0.1 \text{ mol dm}^{-3}$ ) exposed to irradiation at wavelengths above 300 nm was investigated. The rate constant of naphthalene fluorescence quenching by 4-methylpentan-2-one was determined. On the basis of these and other investigations with *cis*-1,3-pentadiene as quencher, as well as the relation between the intensity of light absorbed by naphthalene and that absorbed by ketone in the system studied, it was found that (1) the presence of naphthalene in the range of the concentrations used gives an internal screen effect, (2) 4-methylpentan-2-one, like other aliphatic ketones, quenches the naphthalene singlet state  $S_1$  and (3) in the 4-methylpentan-2-one photolysis the naphthalene acts as sensitizer by singlet-singlet energy transfer and as quencher by triplet-triplet crossing.

### 1. Introduction

Many studies of photosensitization and quenching processes involving ketones have been performed [1 - 3]. Heskins and Guillet [4] state that naphthalene fluorescence is quenched by aliphatic ketones and by an ethylene and carbonyl copolymer (polyketone) and that naphthalene sensitizes the photodegradation of the copolymer.

Continuing these studies Somersall and Guillet [5] have determined a number of rate constants for naphthalene fluorescence quenching by ketones, *e.g.* acetone in various solvents and polyvinylketones. In their recent work on the photolysis of 2-methylpentan-3-one, Abuin and Lissi [6] have assumed, among other things, that "(ii) the naphthalene neither decreases the light absorbed by the ketone (due to an internal screen effect) nor does it increase the number of excited ketone molecules by sensitization". This, together with the assumption that "(iii) the naphthalene does not quench the excited singlet of the ketone", the authors claim to be supported by the results of

their investigation on the type II photocleavage of 4-methylpentan-2-one exposed, in the presence of naphthalene ( $c \leq 0.1 \text{ mol dm}^{-3}$ ) and 1,3-pentadiene, to light of wavelengths greater than 300 nm [7]. Since assumption (ii) and its foundation [6] raise some doubts about the claims of Guillet and co-workers [4, 5], investigations were carried out in this work in an attempt to elucidate the role of naphthalene in the type II photocleavage of 4-methylpentan-2-one (4MP2).

## 2. Experimental

4MP2 (Labor-Chemie, Vienna) was doubly distilled in an argon atmosphere before use and was dried with 4 Å molecular sieves. Naphthalene puriss. (Fluka, Switzerland) was sublimed twice, whilst *cis*-1,3-pentadiene puriss. (Fluka, Switzerland) was used without further purification. *n*-Heptane (Merck, Darmstadt) of "spectroscopic grade", which was used as solvent, was distilled in an argon atmosphere and dried with 5 Å molecular sieves; *n*-hexane (Merck, Darmstadt) of "for fluorescence" quality, which was employed as an internal standard in gas chromatographic determinations, was used without further purification.

The fluorescence spectra ( $\lambda_{\text{exc}} = 313 \text{ nm}$ ) of deaerated solutions of naphthalene and 4MP2 in quartz cells were recorded using a type MPF-3 Perkin-Elmer-Hitachi fluorescence spectrophotometer. The spectra were recorded after taking into account a correction for the exciting light intensity. Spectrophotometric absorption measurements were performed with VSU-2P and UV-VIS Specord spectrophotometers (C. Zeiss, Jena).

Photochemical experiments were performed using a home-built carousel device in thermostatted water ( $20 \pm 0.1 \text{ }^\circ\text{C}$ ). The solutions, deaerated by passing helium through them, were sealed in Pyrex test tubes of inner diameter 3 mm, placed in a rotating holder and exposed to the irradiation emitted by four type Q 81 Original Hanau high pressure mercury lamps through a Pyrex glass layer of total thickness 3 mm. The products of the type II photocleavage of 4MP2 were determined gas chromatographically using a 2.1 m glass column filled with Porapak Q (100 - 120 mesh) at  $182 \text{ }^\circ\text{C}$  and a Pye 105 gas chromatograph equipped with a flame ionization detector.

## 3. Results and discussion

Some of the photophysical properties of naphthalene and 4MP2, which are relevant to the problem investigated in this work, are given in Table 1. The molar decadic absorption coefficient and the energy of the excited singlet state  $S_1$  deserve special attention. The value  $\epsilon_N$  of this coefficient for naphthalene is greater than that  $\epsilon_K$  for 4MP2 by over 20 times at 302 nm and by nearly 20 times at 313 nm. The energy of the singlet state  $S_1$  of naphthalene is slightly greater than that of the singlet state  $S_1$  of 4MP2.

TABLE 1

Some photophysical properties of naphthalene and 4-methylpentan-2-one<sup>a</sup>

Property	Naphthalene	4-Methylpentan-2-one
$\epsilon_{302}$ <sup>b</sup>	278 <sup>c</sup>	12 <sup>d</sup>
$\epsilon_{313}$ <sup>b</sup>	110 <sup>e</sup>	6 <sup>d</sup>
$E_S$ (kcal mol <sup>-1</sup> )	92 <sup>e</sup>	88 <sup>f</sup>
$E_T$ (kcal mol <sup>-1</sup> )	61 <sup>e</sup>	80 <sup>f</sup>
$\phi_{ISC}$	0.80 <sup>e</sup>	0.78 <sup>g</sup>
$\phi_{fl}$	0.20 <sup>e</sup>	10 <sup>-3</sup> <sup>f</sup>
$\tau_s$ (ns)	96 <sup>e</sup>	1.3 <sup>g</sup>

<sup>a</sup>Molar decadic absorption coefficients at 302 nm ( $\epsilon_{302}$ ) and 313 nm ( $\epsilon_{313}$ ); energy  $E_S$  of the singlet state  $S_1$ ; energy  $E_T$  of the triplet state  $T_1$ ; quantum yield  $\phi_{ISC}$  of inter-system crossing; quantum yield  $\phi_{fl}$  of fluorescence; lifetime  $\tau_s$  of the singlet state  $S_1$ .

<sup>b</sup>For a non-polar solvent.

<sup>c</sup>Taken from ref. 8.

<sup>d</sup>Measured in this work.

<sup>e</sup>Taken from ref. 9.

<sup>f</sup>Value measured for acetone [9].

<sup>g</sup>Taken from ref. 7.

Since, in medium pressure and high pressure mercury lamps, the intensity of light of wavelength 313 nm is greater than that of wavelength 302 nm, the problem of light absorption in the naphthalene-4MP2 system can be investigated at 313 nm. Also, at this wavelength the value of  $\epsilon_K/\epsilon_N$  is greater than that at 302 nm.

It is known [10] that the intensity  $I_{abs}^{K(N)}$  of light absorbed by one component, in this case by 4MP2, in the presence of the other absorbing component, in this case by naphthalene, is given by

$$I_{abs}^{K(N)} = I_0 \frac{\epsilon_K c_K}{\epsilon_K c_K + \epsilon_N c_N} \{1 - 10^{-(\epsilon_K c_K + \epsilon_N c_N)l}\} \quad (1)$$

where  $\epsilon_K$  and  $\epsilon_N$  are the molar decadic absorption coefficients for ketone and naphthalene respectively,  $c_K$  and  $c_N$  are the concentrations of ketone and naphthalene respectively,  $I_0$  is the intensity of the incident light and  $l$  is the absorbing path length.

Similarly, the intensity  $I_{abs}^{N(K)}$  of light absorbed by naphthalene in the presence of 4MP2 is given by

$$I_{abs}^{N(K)} = I_0 \frac{\epsilon_N c_N}{\epsilon_K c_K + \epsilon_N c_N} \{1 - 10^{-(\epsilon_K c_K + \epsilon_N c_N)l}\} \quad (2)$$

Dividing eqn. (1) by eqn. (2) results in the equation

$$\frac{I_{abs}^{K(N)}}{I_{abs}^{N(K)}} = \frac{\epsilon_K c_K}{\epsilon_N c_N} \quad (3)$$

The ratio of the intensity of light absorbed by ketone in the presence of naphthalene to that  $I_{abs}^{K,N}$  absorbed by both the ketone and the naphthalene is

$$\frac{I_{\text{abs}}^{\text{K(N)}}}{I_{\text{abs}}^{\text{K,N}}} = \frac{\epsilon_{\text{K}}c_{\text{K}}}{\epsilon_{\text{K}}c_{\text{K}} + \epsilon_{\text{N}}c_{\text{N}}} \quad (4)$$

It can be seen from eqns. (3) and (4) that, in the presence of two absorbing components, the interrelation between the intensity of light absorbed by one component and that absorbed either by the other component or by both components depends on the value of  $\epsilon c$  for each component, but is independent of the absorbing path length.

The ratio of  $I_{\text{abs}}^{\text{K(N)}}$  to  $I_{\text{abs}}^{\text{K}}$  (the intensity of light absorbed by ketone in the absence of naphthalene) is given by

$$\frac{I_{\text{abs}}^{\text{K(N)}}}{I_{\text{abs}}^{\text{K}}} = \frac{\epsilon_{\text{K}}c_{\text{K}} \{1 - 10^{-(\epsilon_{\text{K}}c_{\text{K}} + \epsilon_{\text{N}}c_{\text{N}})l}\}}{(\epsilon_{\text{K}}c_{\text{K}} + \epsilon_{\text{N}}c_{\text{N}})(1 - 10^{-\epsilon_{\text{K}}c_{\text{K}}l})} \quad (5)$$

It can be seen from eqn. (5) that the presence of naphthalene lowers the intensity of light absorbed by the ketone and that this lowering depends on the path length and the concentrations  $c_{\text{K}}$  and  $c_{\text{N}}$ . Only for very low values of  $(\epsilon_{\text{K}}c_{\text{K}} + \epsilon_{\text{N}}c_{\text{N}})l$ , i.e. for a system with nearly 100% transmission, does the intensity value of the light absorbed by 4MP2 in the presence of naphthalene approximate that of the light absorbed by the ketone in the absence of naphthalene. As an example, the interrelations among  $I_{\text{abs}}^{\text{K}}$ ,  $I_{\text{abs}}^{\text{K(N)}}$ ,  $I_{\text{abs}}^{\text{K,N}}$  and  $I_{\text{abs}}^{\text{N(K)}}$  at 313 nm are presented in Table 2 (they are similar to those at 302 nm).

From the data in Table 2 (columns 3, 5 and 8) it can be seen that, in the presence of naphthalene, the intensity of light absorbed by 4MP2 is lower than that absorbed by 4MP2 in the absence of naphthalene for the concentrations  $c_{\text{K}}$  and  $c_{\text{N}}$  and path lengths  $l$  used. Moreover, for  $c_{\text{K}}:c_{\text{N}} = 1:1$  and  $c_{\text{K}}:c_{\text{N}} = 10:1$ ,  $I_{\text{abs}}^{\text{N(K)}}$  is greater than  $I_{\text{abs}}^{\text{K(N)}}$  (columns 5, 6, 7, 10 and 11) and only for  $c_{\text{K}}:c_{\text{N}} = 100:1$  is  $I_{\text{abs}}^{\text{K(N)}}$  greater than  $I_{\text{abs}}^{\text{N(K)}}$ .

Somersall and Guillet [5] have investigated the quenching of naphthalene fluorescence by aliphatic ketones and have found that acetone quenches the naphthalene fluorescence in a non-polar solvent ( $k_{\text{q}} = 4.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). It has been found that the fluorescence of naphthalene ( $c = 0.03 \text{ mol dm}^{-3}$ ) is also quenched by 4MP2 in deaerated *n*-heptane solutions with excitation at 313 nm. After taking into account a correction for the absorption of light of wavelength 313 nm by 4MP2 ( $c = 0.02 - 0.1 \text{ mol dm}^{-3}$ ), given by

$$I_{\text{fl}}^{\text{N}} = I_{\text{fl}}^{\text{N(K)}} \frac{(\epsilon_{\text{N}}c_{\text{N}} + \epsilon_{\text{K}}c_{\text{K}})(1 - 10^{-\epsilon_{\text{N}}c_{\text{N}}l})}{\epsilon_{\text{N}}c_{\text{N}} \{1 - 10^{-(\epsilon_{\text{N}}c_{\text{N}} + \epsilon_{\text{K}}c_{\text{K}})l}\}} \quad (6)$$

the quenching rate constant  $k_{\text{q}}$ , determined using the Stern-Volmer relation, has the value  $2.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Moreover, an increase (by 20 - 30%) in the fluorescence of 4MP2 ( $c = 0.1 \text{ mol dm}^{-3}$ ) at  $\lambda_{\text{exc}} = 313 \text{ nm}$  is observed in the presence of naphthalene ( $c = 0.02 - 0.1 \text{ mol dm}^{-3}$ ) after taking into consideration a correction for the absorption of light of wavelength 313 nm by naphthalene. The measurement of the 4MP2 fluorescence sensitized by naphthalene, however, is not very precise because the fluorescence of the ketone ( $\varphi_{\text{fl}} = 10^{-3}$ ,  $\lambda_{\text{max}} = 400 \text{ nm}$ ) is much disturbed by that of naph-

TABLE 2

Intensity of light absorbed ( $\lambda = 313$  nm) by naphthalene (N) and 4-methylpentan-2-one (4MP2) in *n*-heptane<sup>a</sup>

Solution concentration $c$ (mol dm <sup>-3</sup> )	$l$	$I_{abs}^K \times I_0$	$I_{abs}^N \times I_0$	$I_{abs}^{K(N)} \times I_0$	$I_{abs}^{N(K)} \times I_0$	$I_{abs}^{K(N)} \times I_0$	$I_{abs}^{N(K)} \times I_0$	$I_{abs}^K$ (per cent of $I_{abs}^K$ )	$I_{abs}^N$ (per cent of $I_{abs}^N$ )	$I_{abs}^{K(N)}$ (per cent of $I_{abs}^{K(N)}$ )	$I_{abs}^{N(K)}$ (per cent of $I_{abs}^{N(K)}$ )
4MP2											
1.0	0.1	0.749	0.921	0.346	0.534	0.980	46.19	68.86	35.29	64.70	64.70
	0.3	0.984	0.999	0.353	0.647	0.999	35.85	64.74	35.29	64.70	64.70
	0.5	0.999	0.999	0.353	0.647	0.999	35.29	64.70	35.29	64.70	64.70
1.0	0.01	0.749	0.224	0.680	0.125	0.805	90.85	55.67	84.51	15.49	15.49
	0.3	0.984	0.532	0.839	0.154	0.993	85.22	28.91	84.51	15.49	15.49
	0.5	0.999	0.718	0.845	0.155	0.999	84.49	21.57	84.51	15.49	15.49
0.1	0.1	0.129	0.921	0.048	0.883	0.931	37.20	95.87	5.15	94.84	94.84
	0.3	0.389	0.999	0.052	0.947	0.999	15.26	94.81	5.20	94.79	94.79
	0.5	0.684	0.999	0.052	0.947	0.999	7.55	94.81	5.20	94.79	94.79
0.1	0.01	0.129	0.224	0.114	0.219	0.324	88.37	93.30	35.18	64.81	64.81
	0.3	0.389	0.532	0.244	0.447	0.691	71.94	84.02	35.31	64.68	64.68
	0.5	0.684	0.718	0.303	0.555	0.858	44.27	77.29	35.31	64.68	64.68
0.01	0.01	0.014	0.224	0.012	0.222	0.234	85.71	99.20	5.13	94.87	94.87
	0.3	0.041	0.532	0.028	0.522	0.550	69.51	98.22	5.09	94.90	94.90
	0.5	0.067	0.718	0.038	0.699	0.737	56.71	97.32	5.15	94.84	94.84

<sup>a</sup>For solutions of naphthalene (N) and 4-methylpentan-2-one (4MP2) where  $l$  is the absorbing path length,  $I_{abs}^K$  is the intensity of light absorbed by ketone in the absence of naphthalene,  $I_{abs}^N$  is the intensity of light absorbed by naphthalene in the absence of ketone,  $I_{abs}^{K(N)}$  is the intensity of light absorbed by ketone in the presence of naphthalene,  $I_{abs}^{N(K)}$  is the intensity of light absorbed by naphthalene in the presence of ketone and  $I_{abs}^{K,N}$  is the intensity of light absorbed by ketone and naphthalene.

thalene ( $\varphi_{\text{fl}} = 0.2$ ,  $\lambda_{\text{max}} = 340$  nm). Together with the fluorescence experiments, the type II photocleavage of 4MP2 ( $c = 0.1$  mol dm<sup>-3</sup>) was studied in a solution with no quenchers, in a solution with naphthalene ( $c = 0.02 - 0.1$  mol dm<sup>-3</sup>) or *cis*-1,3-pentadiene ( $c = 0.02 - 0.1$  mol dm<sup>-3</sup>) and in a solution with both naphthalene ( $c = 0.1$  mol dm<sup>-3</sup>) and *cis*-1,3-pentadiene (0.1 mol dm<sup>-3</sup>). The degree of conversion did not exceed 5% in these studies. It can be seen from the results obtained (Table 4) that the concentration of acetone formed during the type II photocleavage of 4MP2 in the solutions containing naphthalene, or naphthalene and *cis*-1,3-pentadiene, is more than twice that in the solutions containing *cis*-1,3-pentadiene alone. This fact can be explained in terms of the estimates made for the absorbing path length, equal to the inner diameter of the test tubes used (0.3 cm) and, for the mean absorbing path length, equal to  $0.3\pi/4$  cm. (Since the irradiation geometry does not ensure parallel beams of light, the actual mean absorbing path length is somewhere between these two values.) The presence of naphthalene ( $c = 0.02 - 0.1$  mol dm<sup>-3</sup>) in the irradiated 4MP2 solution causes a decrease in the intensity of light absorbed by 4MP2 ( $c = 0.1$  mol dm<sup>-3</sup>), *i.e.*  $I_{\text{abs}}^{\text{K(N)}} < I_{\text{abs}}^{\text{K}}$ . Under steady state conditions it is found that

$$I_{\text{abs}}^{\text{N(K)}} = \frac{d[\text{N}^*]}{dt}$$

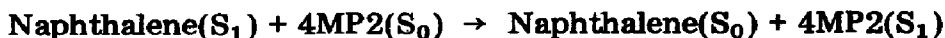
and

$$I_{\text{abs}}^{\text{K(N)}} = \frac{d[\text{K}^*]}{dt}$$

where  $d[\text{N}^*]/dt$  and  $d[\text{K}^*]/dt$  are the formation rates, due to light absorption, of excited molecules in the singlet state  $S_1$  of naphthalene and ketone respectively. Some of the excited naphthalene molecules in the singlet state  $S_1$  react with the naphthalene molecules in the ground state  $S_0$  to form "excimers" [11]. In support of the literature data [11] for methyl derivatives of naphthalene the "excimer" formation rate constant  $k_{\text{ex}}$  can be estimated to be approximately  $1 \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. Furthermore, from the data in Table 1 the fluorescence rate constant  $k_{\text{fl}}$ , calculated from the ratio  $\varphi_{\text{fl}}/\tau_s$ , is  $0.2 \times 10^7$  s<sup>-1</sup> whilst the intersystem crossing rate constant  $k_{\text{ISC}}$ , calculated from the ratio  $\varphi_{\text{ISC}}/\tau_s$ , is  $0.8 \times 10^7$  s<sup>-1</sup>. The rate constant of internal conversion  $k_{\text{IC}}$  can be neglected since the sum of  $\varphi_{\text{fl}}$  and  $\varphi_{\text{ISC}}$  is equal to unity (within the limits of experimental error). On the basis of the constants  $k_{\text{q}}$ ,  $k_{\text{ex}}$ ,  $k_{\text{fl}}$  and  $k_{\text{ISC}}$  the percentage % $N_{\text{q}}$  of excited naphthalene molecules quenched by 4MP2 can be calculated:

$$\%N_{\text{q}} = 100 \frac{k_{\text{q}}[\text{K}]}{k_{\text{fl}} + k_{\text{ISC}} + k_{\text{q}}[\text{K}] + k_{\text{ex}}[\text{N}]} \quad (7)$$

Taking into account the energies of the singlet states  $S_1$  of naphthalene and 4MP2 (Table 1), the quenching process can, with high probability, be assumed to consist of singlet-singlet energy transfer between naphthalene and 4MP2:



Thus, because of the sensitizing action of naphthalene, the number of molecules of ketone in the singlet state  $S_1$  increases and, for a given time interval, is equal to

$$I_{\text{abs}}^{K(N\&N)} = I_{\text{abs}}^{K(N)} + \frac{k_q[K]}{k_{f1} + k_{\text{ISC}} + k_q[K] + k_{\text{ex}}[N]} I_{\text{abs}}^{N(K)} \quad (8)$$

The ratio  $I_{\text{abs}}^{K(N\&N)}/I_{\text{abs}}^{K(N)}$  indicates the increase in the concentration of 4MP2 molecules in the singlet state  $S_1$  due to light absorption by naphthalene compared with that in the same singlet state  $S_1$  in the absence of naphthalene. These values are shown in Table 3.

From the known values of the triplet state  $T_1$  energies of naphthalene and *cis*-1,3-pentadiene ( $E_T = 58.3 \text{ kcal mol}^{-1}$ ) [9] and from the findings of Hammond and Leermakers [12] that naphthalene and *cis*-1,3-pentadiene quench the photoreduction of benzophenone equally effectively, it can be assumed that the quenching of the 4MP2 type II photocleavage from the triplet state  $T_1$  by the two compounds also occurs equally effectively. This leads to the conclusion that the increase in acetone concentration observed in the presence of naphthalene relative to the acetone concentration when *cis*-1,3-pentadiene is used as quencher is caused only by the increased concentration of excited 4MP2 molecules in the singlet state  $S_1$  due to the sensitizing action of naphthalene. The acetone concentrations for 4MP2 solutions containing naphthalene and *cis*-1,3-pentadiene irradiated simultaneously under identical experimental conditions are presented in Table 4.

The error in the chromatographic determinations did not exceed 10%. The values presented in Table 3 (column 9) are in good agreement with the values of the ratio  $C_N^{\text{Ac}}/C_{\text{Pent}}^{\text{Ac}}$  given in Table 4; this is confirmation of the role of naphthalene in the type II photocleavage of 4MP2 proposed in this work.

In summary the following conclusions can be drawn.

(1) The presence of naphthalene in the range of the concentrations employed gives an internal screen effect during the photolysis of 4-methylpentan-2-one, *i.e.* naphthalene decreases the intensity of light absorbed by this ketone.

(2) 4-Methylpentan-2-one, like other aliphatic ketones, is an effective quencher of the naphthalene singlet state  $S_1$ .

(3) In 4-methylpentan-2-one photolysis, the naphthalene acts as sensitizer by singlet-singlet energy transfer and as quencher by triplet-triplet crossing. The contribution of the naphthalene triplet state  $T_2$  of energy  $E_T = 88 \text{ kcal mol}^{-1}$  can be neglected since the lifetime of this state is only 12 ps [13].

These conclusions are in accord with the results obtained by Guillet and coworkers [4, 5].

TABLE 3

Intensity of light absorbed ( $\lambda = 313$  nm) by 4-methylpentan-2-one (4MP2) as a function of naphthalene (N) concentration taking sensitization into consideration<sup>a</sup>

Solution concentration $c$ (mol dm <sup>-3</sup> )	$l$ (cm)	$I_{\text{abs}}^{\text{K}} \times I_0$	$I_{\text{abs}}^{\text{K(N)}} \times I_0$	$I_{\text{abs}}^{\text{N(K)}} \times I_0$	$I_{\text{abs}}^{\text{K,N}} \times I_0$	$I_{\text{abs}}^{\text{K(tN)}} \times I_0$ (per cent of $I_{\text{abs}}^{\text{N(K)}}$ )	$I_{\text{abs}}^{\text{K(NtN)}} \times I_0$	$\frac{I_{\text{abs}}^{\text{K(NtN)}}}{I_{\text{abs}}^{\text{K}}}$
4MP2	N							
0.1	0.02	0.389	0.183	0.672	0.855	89.83	0.787	2.32
	0.3 $\pi$ /4	0.278	0.167	0.614	0.781	89.83	0.719	2.58
0.1	0.04	0.339	0.116	0.852	0.968	84.13	0.833	2.45
	0.3 $\pi$ /4	0.278	0.212	0.822	0.934	84.13	0.803	2.89
0.1	0.06	0.339	0.083	0.910	0.993	79.10	0.803	2.37
	0.3 $\pi$ /4	0.278	0.082	0.898	0.980	79.10	0.792	2.85
0.1.	0.1	0.339	0.052	0.947	0.999	70.66	0.721	2.13
	0.3 $\pi$ /4	0.278	0.052	0.946	0.998	70.66	0.720	2.59

<sup>a</sup> $I_{\text{abs}}^{\text{K(NtN)}} (= I_{\text{abs}}^{\text{K(N)}} + I_{\text{abs}}^{\text{K(N)N(K)}})$  is the total intensity of light absorbed by ketone in the presence of naphthalene as a result of direct absorption ( $I_{\text{abs}}^{\text{K(N)}}$ ) and "transfer" from naphthalene excited molecules to ketone molecules ( $I_{\text{abs}}^{\text{K(N)N(K)}}$ ), i.e. the number of excited ketone molecules in the singlet state  $S_1$  in a given time interval as a result of direct absorption of light and the sensitizing action of naphthalene.



TABLE 4

Concentration of acetone formed during type II photocleavage of 4-methylpentan-2-one in the presence of *cis*-1,3-pentadiene (Pent) and naphthalene (N)

Concentration (mol dm <sup>-3</sup> ) of Pent and N		Concentration <i>c</i> (mmol dm <sup>-3</sup> ) of acetone for two irradiation times		$C_N^{Ac}/C_{Pent}^{Ac}$ for two irradiation times <sup>a</sup>	
		5 min	10 min	5 min	10 min
0.00	(Pent and N)	2.6	4.6		
0.02	(Pent)	0.7	1.1	2.28	2.18
	(N)	1.6	2.4		
0.04	(Pent)	0.6	1.0	2.50	2.63
	(N)	1.5	2.5		
0.06	(Pent)	0.5	0.9	2.60	2.55
	(N)	1.3	2.3		
0.1	(Pent)	0.6	1.0	2.66	2.40
	(N)	1.6	2.4		
	(Pent and N)	1.5	2.4	2.50	2.40

<sup>a</sup> $C_N^{Ac}/C_{Pent}^{Ac}$  is the ratio of the concentration of acetone formed in the presence of naphthalene to that formed in the presence of *cis*-1,3-pentadiene.

### Acknowledgment

The author is grateful to Professor Jan Wojtczak for his valuable remarks made during a discussion of the results.

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