THE ROLE OF EXCITED STATES IN THE PHOTOLYSIS OF *n*-BUTYRALDEHYDE, I.

Triplet State Quenching by Piperylene

By

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Experimental techniques suitable-for the study of the role played by excited states in the photolysis of *n*-butyraldehyde are described. Preliminary experimental results obtained with piperylene quencher in the vapor phase and isooctane are given, and the contributions of the excited singlet and triplet states in the four major primary photochemical processes of *n*-butyraldehyde photolysis at 313 nm were estimated.

Introduction

A detailed study of the vapor phase photolysis of *n*-butyraldehyde was made by BLACET and CALVERT [1, 2] which elucidated most of the major photochemical primary and secondary processes. Although recent work carried out in our laboratory [3] showed the nature of primary reactions and the mechanism of secondary processes to be more complex than originally assumed by BLACET and CALVERT nevertheless the basic mechanistic features of the photolysis seem to be fairly well established. However, much less is known of the role played by the excited singlet and triplet states in the photolysis of *n*-butyraldehyde. Most of the investigations in this field dealt with excited state precursors of only one or two primary photochemical processes—often only with those involved in the NORRISH type II elimination—and the conclusions were of qualitative nature.

Vapor phase experiments have definitely proved that both NORRISH type I decomposition into *n*-propyl and formyl radicals and type II ethylene elimination may occur from the triplet state.

On the basis of the very low yield of ethylene obtained in the mercury-sensitized decomposition of *n*-butyraldehyde as compared to the direct photolysis, BORRELL and NORRISH suggested [4] that only excited singlet molecules can undergo type II elimination. However, in a later paper NORRISH and WAYNE showed [5] the failure of BORRELL and NORRISH to detect the type II products in the sensitized reaction to be caused by the consumption of the ethylene in secondary reactions during extended photolysis.

BORKOWSKI and AUSLOOS [6] investigated the vapor phase fluorescence and its relationship to the photolysis of *n*-butyraldehyde. They could show that the fluorescence emitted by butyraldehyde was not affected by the addition of biacetyl,

however, a strong emission — ascribed to triplet excited biacetyl formed in a triplet energy transfer process — was observed. At 334 nm, biacetyl reduced the relative rate of C_2H_4 formation by nearly a factor of ten, but did not appreciably affect the yield of propane. On the basis of these observations it was concluded that an excited triplet aldehyde molecule is involved in the type II elimination and the type I decomposition occurs from a singlet electronic state and/or from a triplet electronic state excited to a high vibrational level.

The investigations of REBBERT and AUSLOOS [7] at 313 nm wavelength showed that both type I and type II decomposition of n-butyraldehyde can be photosensitized by acetone. On the basis of luminescence measurements it was suggested that an aceton molecule can transfer its triplet-state energy to form a triplet excited aldehyde molecule. Consequently, the results on the sensitized decomposition of n-butyraldehyde may be taken as evidence for the occurrence of type I and type II reactions from the triplet state of the aldehyde.

The effect of cis-butene-2 and biacetyl on the vapor phase photolysis of n-butyraldehyde at 313 nm has been investigated by CUNDALL and DAVIES [8]. Since both dissociation and ethylene elimination was quenched at 321 K by biacetyl and by cis-butene-2 (and simultaneous isomerization of the latter compound occurred) it was concluded that type I and type II processes occur through a triplet state. (However, the possibility of contribution to the type I reaction from the singlet state was not excluded.) On the basis of observed relative quenching efficiency of biacetyl and cis-butene-2, it was suggested that type I and type II reactions occur from upper and lower vibrational levels of the triplet state, which are however similar (not far) in energy.

Information available on the role of the excited states in solution is less detailed than in the vapor phase. The photolysis of n-butyraldehyde in solution was studied by COYLE [9]. Relative quantum yields for type II product and for cyclobutanol formation in benzene were reported. Piperylene was used to quench reactions occurring from the triplet state. It was found that part of the photochemical reaction was quenched efficiently and part was relatively unaffected. Hence, it was concluded that reaction occurs to an appreciable extent from both the $n\pi^*$ triplet and the $n\pi^*$ singlet states, respectively. From the slopes of STERN—VOLMER plots, a triplet-state lifetime of $3.5 \cdot 10^{-8}$s was obtained.

Recently LEBOURGEOIS et al. [10] published a paper on the photochemical behaviour of n-butyraldehyde in solution. Conclusions were drawn from measurements of absorption, fluorescence and aldehyde consumption; product analysis was not attempted. Naphtalene quenching experiments were made to show that the triplet state is responsible for the major part of the photochemical reactions. The quantum yield for reactions occurring from the singlet excited state was estimated to be less than 0.14. It was suggested that at n-butyraldehyde concentrations less than 10^{-1} mol $\cdot$ dm^{-3} the singlet-state molecules react in unimolecular reactions, while at higher concentrations the reaction of an excited singlet and a ground state aldehyde molecule dominates. The triplet state was assumed to be consumed in a bimolecular reaction — in an interaction between a triplet excited and a ground state butyraldehyde molecule — yielding a pair of butyryl and hydroxybutyl radicals which recombine to form an acetoin homologue. LEBOURGEOIS et al. estimate the lifetime of the excited singlet state to be $6 \cdot 10^{-10}$s at low aldehyde concentrations. The triplet-state lifetime was shown to decrease with increasing aldehyde concentra-

tion in the range of 10^{-2} to 10^{-1} mol·dm^{-3}; the lifetime values reported were around 10^{-8}s.

Survey of the information available in literature on the nature of the excited-state precursors of the various primary photochemical products of *n*-butyraldehyde shows that further quantitative data are required in particular for the relative singlet and triplet contributions to the individual primary processes, and for the energies and lifetimes of the excited states from which these reactions occur. A systematic study of these questions, both in the vapor phase and in solution, has been initiated in our laboratory. In this paper we present the preliminary results obtained with *cis*-piperylene (*cis*-pentadiene-1,3), generally known as an efficient quencher of the triplet states of carbonyl compounds.

Experimental

Materials

The *n*-butyraldehyde obtained from FLUKA AG was purified by precipitation with sodium hydrogen sulfite. The recovered aldehyde (generated in nitrogen atmosphere) was dried over anhydrous magnesium sulfate and further purified by repeated distillation *in vacuum*, only the middle fractions being retained. The purified sample contained about 0.5 percent isobutyraldehyde as determined by gas liquid chromatography; the amount of other impurities was around the detection limit of the flame ionization detector. The aldehyde was stored in dark *in vacuum*, in a flask closed with a greaseless polyethylene valve.

The *cis*-piperylene (FLUKA AG) was 99.6 percent pure, containing 0.4 percent *trans* isomer. Purification consisted of repeated bulb-to-bulb distillation *in vacuum*. The sample was stored in dark in a vessel equipped with a YOUNG valve (teflon sealing).

The isooctane used as solvent was obtained from FLUKA AG. Purification was carried out by distillation on a high performance column (theoretical plate number over 10). Only a middle fraction, shown to contain saturated C_8 and some C_7 hydrocarbons, was used.

Isopentane used as an internal standard was obtained from KOCH and LIGHT. The purification procedure was identical with that described for isooctane.

Apparatus and methods

The method used in the experiments may be divided in four working processes:

(i) Preparation of the sample to be irradiated;
(ii) Irradiation and light intensity measurement;
(iii) Preparation of the sample for analysis;
(iv) Analysis.

The first three working processes were somewhat different in case of the vapor phase investigations and in the experiments made in solution and require detailed description, while the method of analysis applied in the vapor phase and solution experiments was the same.

Preparation of the aldehyde vapor samples to be irradiated

The sample was prepared by direct evaporation of the components into the evacuated reaction vessel (irradiation cuvette). Pressures were measured with a quartz spiral-manometer (BODENSTEIN type) which was used as a null-instrument. The sample was left to stand 30 minutes to attain complete mixing of the components before irradiation.

Vapor phase irradiation and intensity measurement

The vapor phase experiments were carried out in a cylindrical quartz cell of 4.5 cm internal diameter and 8.0 cm length, equipped on both ends with sealed ultrasil planparallel windows. The cell was attached to a vacuum apparatus through a greaseless polyethylene valve. Temperature was kept constant by means of a thermostating jacket through which silicon oil from a thermostat was circulated.
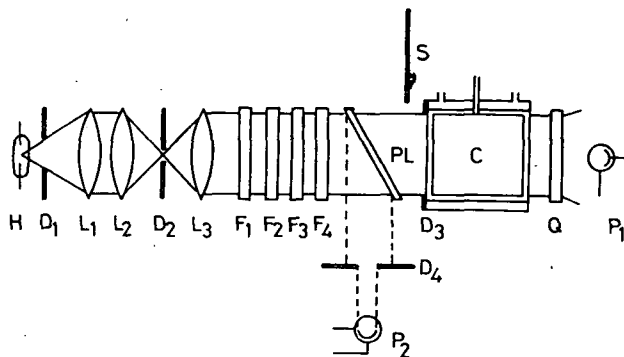

Fig. 1. Diagram of the irradiation line
(For the designations see the text.)

The irradiation line, installed on an optical bench, is shown in Fig. 1. The light source H was an OSRAM HBO—500 high pressure mercury arc mounted in a metal house. The ultrasil quartz lenses L_1, L_2 and L_3 as well as the diaphragms D_1 and D_2 served to obtain a nearly parallel but slightly convergent beam. A third diaphragm D_3 cut the cross-section of the beam to the size which ensured that the light filled the irradiation cell C almost completely. Irradiation could be started or interrupted by moving the shutter S.

A band in the 313 nm region was isolated using a combination of four filters, F_1—F_4, which are described in Table I. The light emerging from the filter combination showed a width of 3 nm at the half height of the band.

The light intensities were measured by means of a PRESSLER DGL 490a vacuum photocell P_1 which was placed behind the reaction cell C. The photocell was connected to a 100V high-stability DC power supply unit and the signal, after amplification, could be either red or recorded. In order to reduce the light intensity

Table I

Filter combination used to isolate a band in the 313 nm region

Designation of the filter	Optical depth in mm	Description of the filter
F_1	25	64 g $NiSO_4 \cdot 6\,H_2O$ + 10 g $CoSO_4 \cdot 6\,H_2O$ + + 100 cm³ H_2O
F_2	25	$5 \cdot 10^{-4}$ mol·dm⁻³ K_2CrO_4
F_3	10	0.0245 mol·dm⁻³ $KHC_8H_4O_4$
F_4	4	UG 11 (SCHOTT, Jena)

to the level required by the photocell, a fluorescent screen Q was placed between C and P_1. This was similar to PARKER's quantum counter [11], and consisted of a cell of 10 mm optical depth containing a solution of $1.1 \cdot 10^{-3}$ mol·dm⁻³ fluorescein, 0.5 N sodium carbonate and 0.05 N sodium bicarbonate. The whole quantum counter system was calibrated by means of a ferrioxalate actinometer. The calibration was shown to be linear in the light intensity range used by us for irradiation ($2 \cdot 10^{-11}$ to $3 \cdot 10^{-9}$ einstein·cm⁻²·s⁻¹). In the calculation of the quantum yields, measured intensities were corrected for the reflexion on the optical surfaces.

Much attention was paid to use stable light intensity during irradiation. Therefore a power supply unit was developed for the mercury arc which could be used in (*i*) voltage stabilized-, (*ii*) current stabilized-, (*iii*) light intensity stabilized-, and (*iv*) externally controlled working mode. In quantitative photochemical investigations, the light intensity stabilized mode was used, and a controlling system kept the light intensity of the mercury arc constant at a pre-set value.

The controlling system consisted of the mercury arc H, the power supply unit and a photocell P_2 (type DGL 490*a*, Deutsche Glimmlampengesellschaft PRESSLER, Leipzig). A fraction of the exciting radiation was reflected by a planparallel quartz plate PL onto the cathode of the photocell P_2. An error signal, the difference between the photocell current and the pre-set current proportional to the required light intensity, was used to control the power supply unit of the mercury arc.

With this controlling system the long range drift of the intensity of the exciting light was kept within ±2 percent. The short range stability was better than the accuracy of the readings, corresponding to about ±0.2 percent of the intensity.

Preparation of the irradiated vapor phase samples for analysis

After irradiation, the reaction cell was attached to a vacuum line, the gas mixture was led through a trap cooled to liquid air temperature, and the non-condensable products were collected by a TOEPLER pump and their volume was measured in a gas burette. The products condensable at liquid air temperature were dissolved in isooctane containing isopentane and cyclohexanone as internal standards which was introduced previous to the whole procedure into a small tube attached to the bottom of the trap. Finally, the small tube containing the solution of the products was sealed off. Both the gas and the solution sample was analysed by gas chromatography.

Preparation of the solution samples to be irradiated

The isooctane solvent containing isopentane as internal standard was carefully degassed. Then solutions of *n*-butyraldehyde and of piperylene, respectively, were prepared in two separate vacuum lines by freezing known amounts of these compounds on the top of given volumes of the solvent. These solutions as well the solvent were used to prepare a set of samples in which the concentration of the aldehyde and that of the internal standard was constant but the concentration of piperylene varied. The cylindrical Uviol cuvettes (1.2 cm internal diameter) containing the solution samples were sealed off, detached from the vacuum line and subjected to irradiation.

Irradiation of the solution samples

A series of solution samples with varying piperylene concentration were irradiated simultaneously. Two methods, termed method *A* and method *B* were used.

In method *A*, the optical line was similar to that used in the vapor phase irradiations (see Fig. 1.) except for the design of the reaction cell and the thermostating jacket. A cuvette holder drum accomodating 12 cuvettes was rotating at the end of the optical line. Thus, all the samples absorbed the same number of ligh quanta. The cuvette holder drum was enclosed in a cylindrical vessel which could serve as an air or liquid thermostat. There was a quartz window on the vessel where the light beam entered.

In method *B*, a rotating mercury arc (a 125W PHILIPS medium pressure arc connected to a current stabilized DC power supply unit) was surrounded by 8 sample cuvettes. The Uviol cuvettes were mounted vertically on a fixed base parallel to and in equal distances from the central mercury arc. The arc was surrounded by a spherical filter jacket (optical depth = 2.5 cm), made of Uviol glass, through which a filter solution circulated. The filter solution which isolated a band in the 313 nm region was prepared by dissolving 32 g $NiSO_4 \cdot 6H_2O + 10g$ $CoSO_4 \cdot 6H_2O + 0.5g$ $KHC_8H_4O_4$ in 100 cm^3 water. Because of the decomposition of the potassium hydrogen phtalate on irradiation, the filter solution had to be replaced in each experiment. The spectral distribution of the exciting light in this set-up may be characterized by 1.5 nm width at the half height of the band.

Preparation for analysis of the irradiated solution samples

In experiments where analysis of the CO product was not made, no special preparation of the sample was required. The cuvette was opened, the second internal standard (cyclohexanone) was added and the sample was ready for analysis.

In the rest of the experiments the cuvette equipped with a break seal was attached to a vacuum line, the break seal was opened and the whole content was distilled into a trap kept at liquid air temperature. The non-condensable products were collected by a TOEPLER pump and their volume was measured in a gas burette. The condensable products were sealed into a small tube attached to the bottom of the trap. Both gas and liquid samples were analysed by gas chromatography.

Analysis

Product analysis was carried out on a HEWLETT—PACKARD type 5751G and a CARLO—ERBA Linea DACI gas chromatograph. Nitrogen carrier gas was used and flame ionization detection was generally applied, except for the hydrogen measurements (thermal conductivity detector). Peak areas were measured (using a HEWLETT—PACKARD type 3370B digital integrator) against that of an internal standard (either isopentane or cyclohexanone) or against the peak area of a product the amount of which in the sample was already known from another analysis. Altogether four columns were required for the detailed quantitative analysis of the composition of the irradiated samples:

   (*i*) 2.5 m Molecular Sieve 5A, stainless steel tube of 6 mm i.d.;
   (*ii*) 1.8 m Alumina, stainless steel tube of 6 mm i.d.;
   (*iii*) 3.0 m Porapak QS deactivated with 0.5 percent Apiezon L, stainless steel tube of 2.5 mm i.d.;
   (*iv*) 30 m SCOT column with Carbowax 20M stationary phase, 0.25 mm i.d.
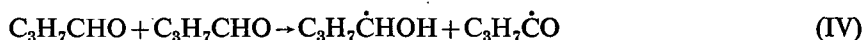
The non-condensable gas fraction was analysed for hydrogen on the Molecular Sieve column at 343 K, and for methane on the Alumina column at 373 K. The amount of CO was obtained from the volume of the gas fraction measured in the gas burette by taking into account the H_2 and CH_4 content.

The liquid fraction (condensable at liquid air temperature) was analysed for ethane, ethylene, propane and propylene on the Alumina column at 373 K; ethylene, propane, piperylene, *n*-butyraldehyde and *n*-hexane were measured against isopentane internal standard on the Porapak QS column at 443 K. Finally, *n*-butanol, cyclobutanol, 4-heptanol and 4-heptanone were analysed on the SCOT column at 383 K using cyclohexanone as internal standard.

Results and discussion

In the investigations described in this paper, the role of the excited singlet and triplet states of the aldehyde molecule in the major primary photochemical processes of *n*-butyraldehyde photolysis was studied by observing the effect of piperylene on the quantum yields of certain products characteristic for the primary processes dealt with.

A detailed study of the photolysis of *n*-butyraldehyde is in progress in our laboratory [3], and the results obtained so far show that seven more or less important primary processes occur at 313 nm both in the vapor phase and in isooctane solution. The major ones are

$$C_3H_7CHO \rightarrow \dot{C}_3H_7 + \dot{C}HO \qquad \qquad \text{(I)}$$

$$C_3H_7CHO \rightarrow C_2H_4 + CH_3CHO \qquad \qquad \text{(II)}$$

$$C_3H_7CHO \rightarrow \text{cyclobutanol} \qquad \qquad \text{(II}')$$

$$C_3H_7CHO + C_3H_7CHO \rightarrow C_3H_7\dot{C}HOH + C_3H_7\dot{C}O \qquad \qquad \text{(IV)}$$

Two of these (*i.e.* the NORRISH type II decomposition and the rearrangement step II′) yield stable products. On the other hand the NORRISH type I decomposition into *n*-propyl and formyl radicals, and the reaction of an excited state and a ground state aldehyde molecule forming hydroxybutyl and *n*-butyryl radicals are followed by secondary processes.

If a primary process occurs from two excited states and one of them (*i.e.* a triplet state) is quenched and the other (*i.e.* an excited singlet state) is unaffected by a quencher, then the contributions of the quenchable and unquenchable states can be given by

$$\eta^{T} = (\Phi^0 - \Phi^\infty)/\Phi^0 \tag{1}$$

and

$$\eta^{S} = \Phi^\infty/\Phi^0 \tag{2}$$

where Φ^0 and Φ^∞ designate the quantum yields of a primary product obtained in the absence of the quencher and at a quencher concentration high enough to deactivate completely the quenchable state, respectively. For reactions II and II′ the primary products can be measured directly in the irradiated sample, thus η^T and η^S are obtained in a straightforward manner. However, this is not the case for reactions I and IV where only the products formed in secondary free radical reactions can be measured. Nevertheless, if certain conditions are fulfilled, some secondary products might be found, the quenching characteristics of which supply information on the role played by various excited state precursors.

The choice of the characteristic product quantum yields to be used in equ. (1) and (2) in order to calculate η^T and η^S, respectively, for reactions I and IV, requires careful consideration of the kinetics and the stoichiometry of the secondary free radical processes. Important points on which special emphasis should be laid are the following:

(*i*) If reaction chains are involved in the formation of the secondary products, then quenchers are expected to alter considerably the chain length and the stoichiometry of the reaction, therefore simple correlation does usually not exist between product quenching and the contribution of the various excited states to the particular primary process.

(*ii*) Assuming that chains do not occur or chain length is very short, nevertheless the stoichiometry of the reaction changes on addition of a quencher if the radical formed in the primary process is consumed in competitive elementary steps among which some are first and others are second order with respect to the free radical. In such cases information on the role played by the various excited state precursors can be obtained from quenching plots where the weighted sum of the quantum yields of all (or all significant) products formed in the reactions of the primary free radical are plotted against the quencher concentration.

(*iii*) In the simplest case where the quencher does not alter the reaction stoichiometry, any product may be chosen as the characteristic one. Thus, the quantum yields of any product may be used to obtain η^T and η^S by means of equ. (1) and (2), respectively.

(*iv*) In the case considered above it has been tacitly assumed that only physical quenching (triplet energy transfer) occurs. However, if the quencher reacts with the free radicals, then chemical quenching of the reactive intermediates is superimposed upon the physical quenching of the excited state precursor, causing an overestimation of the role played by the quenchable excited state.

A study of secondary photochemical processes in the gas and liquid phase photolysis of *n*-butyraldehyde at 313 nm, carried out in our laboratory (see [3] and subsequent papers), revealed that the mechanism is complex. Chains occur in the vapor phase photolysis, however the chain length is short (less than 1.3) at room temperature. The information (see [3] and subsequent papers) available on the mechanism of the free radical processes following reactions I and IV demand that η^T and η^S be obtained from quenching plots where the weighted sum of the quantum yields of all significant products formed in the reactions of the appropriate primary radical are taken into account (compare with paragraph ii above).

Table II and III give the product quantum yields measured by us in the vapor

Table II

Product quantum yields obtained in the gas phase without added piperylene at 313 nm wavelength and room temperature. $[C_3H_7CHO]_0 = 2.7 \cdot 10^{-3}$ *mol·dm*$^{-3}$; $I_0 = 6.5 \cdot 10^{-10}$ *einstein·cm*$^{-2} \cdot s^{-1}$

C_2H_4	CH_3CHO	Cyclo-butanol	CO	C_3H_8	C_6H_{14}	C_3H_6	4-Hepta-none	4-Hepta-nol	*n*-Bu-tanol
0.17	0.18	0.032	0.43	0.29	0.093	0.019	0.004	0.008	0.010

phase and in isooctane, respectively. The two sets of quantum yields shown in Table III were obtained by method *A* and *B* at considerably different intensities. Products of very little importance (see [3]) are not included in the tables. The results clearly show that the same products are formed in the vapor phase and in isooctane.

Table III

Product quantum yields obtained in isooctane without added piperylene at 313 nm wavelength and room temperature. $[C_3H_7CHO]_0 = 1 \cdot 10^{-2}$ *mol·dm*$^{-3}$; $^{a)}I_0 = 2.8 \cdot 10^{-10}$ *einstein·cm*$^{-2} \cdot s^{-1}$ *(Method A);* $^{b)}I_0 = 5.0 \cdot 10^{-9}$ *einstein·cm*$^{-2} \cdot s^{-1}$ *(Method B)*

	C_2H_4	CH_3CHO	Cyclo-butanol	CO	C_3H_8	C_6H_{14}	C_3H_6	4-Hepta-none	4-Hepta-nol	*n*-Bu-tanol
Φ^0 $^{a)}$	0.13	0.14	0.034		0.29	0.010	0.006	0.012	0.027	0.059
Φ^0 $^{b)}$	0.12	0.12	0.043	0.17	0.19	0.011	0.010	0.011	0.029	0.085

Ethylene and acetaldehyde are the products of the NORRISH type II decomposition of *n*-butyraldehyde, and the presence of cyclobutanol among the products both in the vapor phase and in isooctane indicates the occurrence of reaction II'. The C_2H_4 or CH_3CHO and the cyclobutanol are primary products characteristic for primary reactions II and II', respectively.

Butyraldehyde decomposition according to reaction I gives formyl and *n*-propyl radicals. The subsequent reactions of the formyl radicals yield carbon monoxide as the sole significant product both in the vapor phase and in isooctane, thus the type I decomposition may be characterized by the measurement of CO formation. Reactions of the *n*-propyl radicals give various reaction products. It may be shown (see [3] and subsequent papers) that the predominant part of the propyl radicals is recovered in the form of C_3H_8, C_6H_{14} and C_3H_6. A minor part of the propyl radicals is consumed in the vapor phase in reactions leading to the formation of hepta-4-one and hepta-4-ol. (It is to be noted, however, that in solution the latter compounds are formed by other routes.) Since 4-heptanone and 4-heptanol are minor products of negligible importance from our point of view, the characteristic type I product quantum yield can be expressed as the weighted sum $\Phi_{C_3H_8} + 2\Phi_{C_6H_{14}} + \Phi_{C_3H_6}$. (A factor of 2 appears before the *n*-hexane quantum yield because two C_3H_7 radicals are consumed in the formation of a C_6H_{14} molecule.)

Secondary processes of the hydroxybutyl radical formed in reaction IV give 4-heptanol and *n*-butanol. Other products formed in hydroxybutyl radical reactions were detected [3] but are of little importance under the conditions of our investigations. Thus one may suggest the sum $\Phi_{4\text{-heptanol}} + \Phi_{n\text{-butanol}}$ as the quantum yield characteristic for reaction IV.

The quenching plots for the type II products obtained in the vapor phase and in solution are shown in Fig. 2 and 3, respectively. The yields of C_2H_4 and CH_3CHO
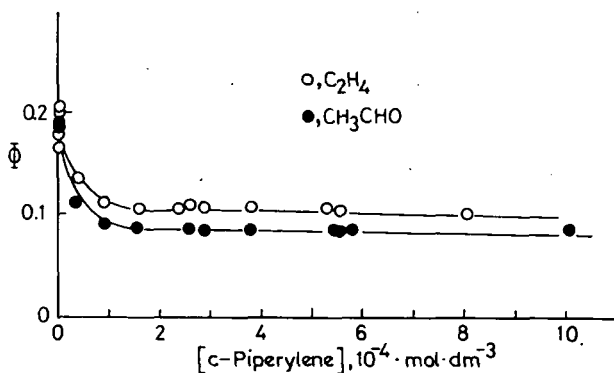

Fig. 2. Quenching plots of ethylene and acetaldehyde in the vapor phase. $T = 298$ K, $[C_3H_7CHO] = 2.7 \cdot 10^{-3}$ mol·dm^{-3}, $\lambda = 313$ nm, $I_0 = 6.5 \cdot 10^{-10}$ einstein·cm^{-2}·s^{-1}

agree in solution both in the absence and in the presence of the quencher. However, there is a minor disagreement (exceeding the error limits) apparent in the vapor phase, for which satisfactory explanation has not been found so far. The quantum yields decrease with increasing quencher concentration and seem to attain a limiting value at around 10^{-4} and 10^{-3} mol·dm^{-3} piperylene concentrations in the vapor phase and in isooctane, respectively. If the residual reaction is assumed to occur from the singlet excited state and the quenchable part from the triplet state, then one obtains with equ. (1) and (2) for the triplet and singlet state contributions,

respectively, to the type II decomposition: $\eta^T=0.45$ and $\eta^S=0.55$ (vapor phase), $\eta^T=0.75$ and $\eta^S=0.25$ (solution).

The results on the quenching of the cyclobutanol formation by piperylene in the vapor phase and in solution are shown in Fig. 4. and 5., respectively. Again the quen-
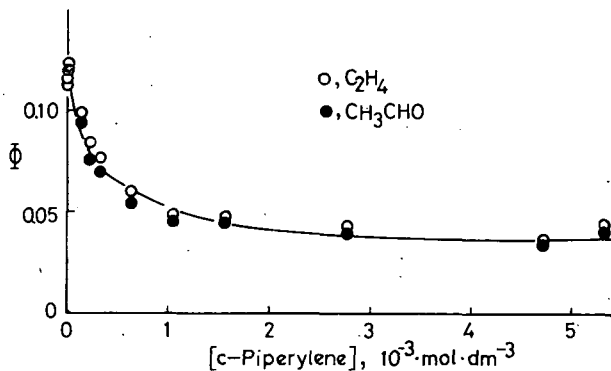

Fig. 3. Quenching plots of ethylene and acetaldehyde in iso-octane. $T=298$ K, $[C_3H_7CHO]_0=1\cdot10^{-2}$ mol·dm^{-3}, $\lambda=313$ nm, $I_0=5.0\cdot10^{-9}$ einstein·cm$^{-2}\cdot$s^{-1}
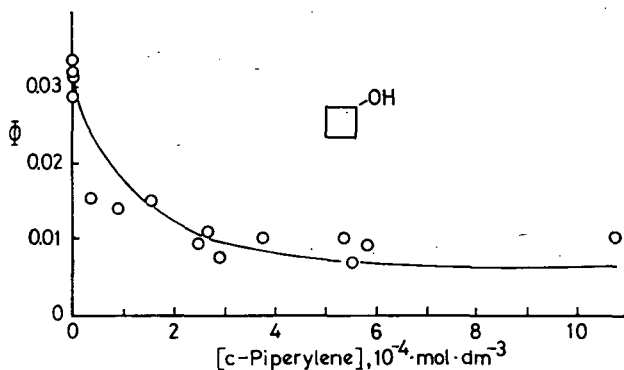
Fig. 4. Quenching of cyclobutanol formation in the vapor phase. $T=298$ K, $[C_3H_7CHO]_0=2.7\cdot10^{-3}$ mol·dm^{-3}; $\lambda=313$ nm, $I_0=6.5\cdot10^{-10}$ einstein·cm$^{-2}\cdot$s^{-1}

ching curves seem to level off above 10^{-4} and 10^{-3} mol·dm^{-3} in the vapor phase and in isooctane, respectively. Assuming that, at high quencher concentrations, cyclo-butanol formation originates from the excited singlet state, one obtains for the contribution of the two excited state precursors $\eta^T=0.80$ and $\eta^S=0.20$ in the vapor phase, and $\eta^T=0.80$ and $\eta^S=0.20$ in isooctane.

Quenching of carbon monoxide, propane, *n*-hexane and propylene formation by piperylene in the vapor phase and in solution is shown in Fig. 6 and 7, respectively.
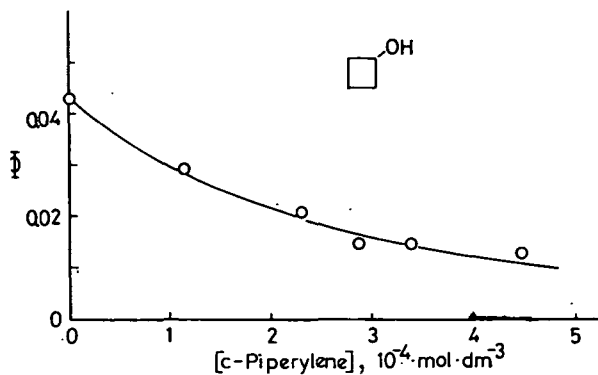
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Fig. 5. Quenching of cyclobutanol formation in isooctane.
$T = 298$ K, $[C_3H_7CHO]_0 = 1 \cdot 10^{-2}$ mol·dm^{-3}, $\lambda = 313$ nm,
$I_0 = 5.0 \cdot 10^{-9}$ einstein·cm^{-2}·s^{-1}

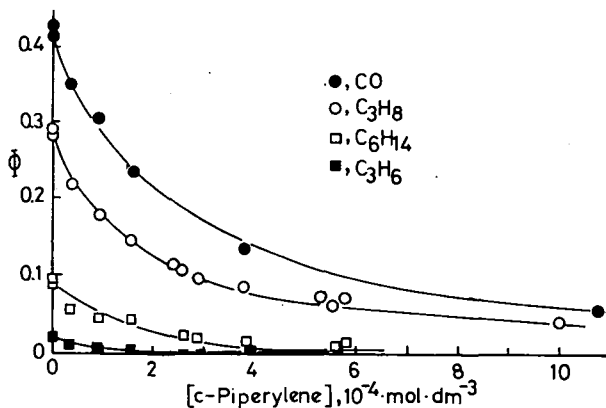*Fig. 6.* Quenching of CO, propane, *n*-hexane and propylene
formation in the vapor phase. $T = 298$ K, $[C_3H_7CHO]_0 = 2.7 \cdot 10^{-3}$
mol·dm^{-3}, $\lambda = 313$ nm, $I_0 = 6.5 \cdot 10^{-10}$ einstein·cm^{-2}·s^{-1}
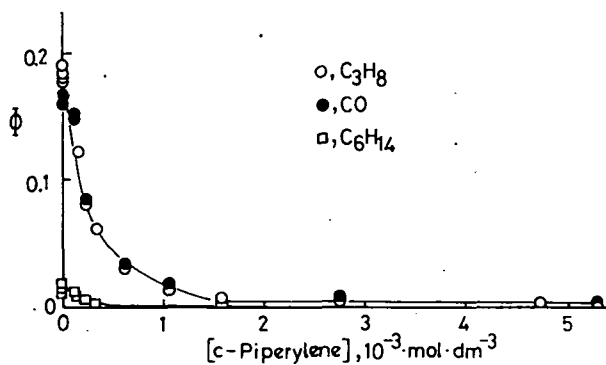
Fig. 7. Quenching of CO, propane and *n*-hexane formation in
isooctane. $T = 298$ K, $[C_3H_7CHO]_0 = 1 \cdot 10^{-2}$ mol·dm^{-3}, $\lambda = 313$ nm,
$I_0 = 5.0 \cdot 10^{-9}$ einstein·cm^{-2}·s^{-1}

It may be seen from the figures that the formation of the products related to the type I decomposition is influenced to a great extent by piperylene, indicating the significant role played by the triplet state in the NORRISH type I decomposition. This is true especially for the reaction occurring in isooctane. The change in stoichiometry with increasing piperylene concentration is also apparent from the figures. (Note that the quantum yield of *n*-hexane formation decreases more rapidly than that of propane.)

In Fig. 8 and 9 the relative quenching plots of characteristic type I product quantum yields are shown for the vapor phase and for isooctane solution, respectively. It is important to note that the relative quenching curves based on the sum $C_3H_8 + 2C_6H_{14} + C_3H_6$ agree within the limits of experimental error with those obtained from CO measurements. This supports our choice made for expressing the characteristic product quantum yield. The quenching curves suggest that $\eta^T > 0.80$ and
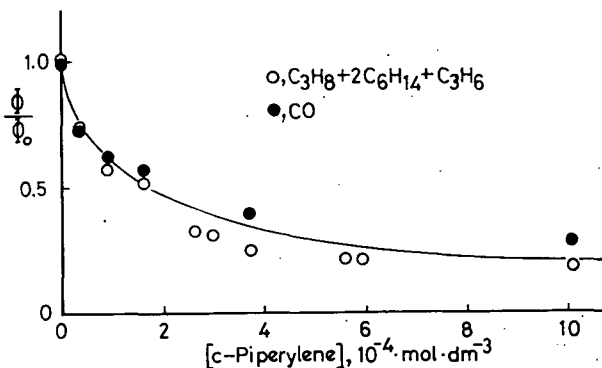

Fig. 8. Relative quenching plot of the characteristic type I product quantum yields Φ_{CO} and $(\Phi_{C_3H_8} + 2\Phi_{C_6H_{14}} + \Phi_{C_3H_6})$, in the vapor phase
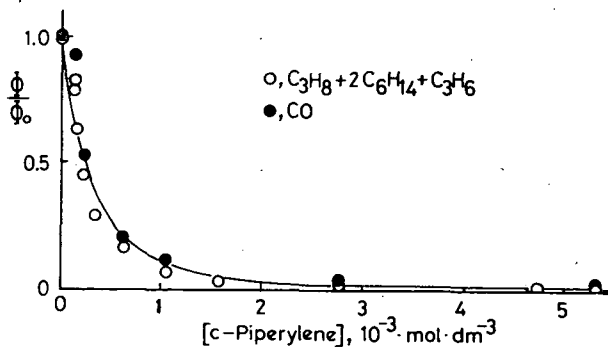

Fig. 9. Relative quenching plot of the characristic type I product quantum yields, Φ_{CO} and $(\Phi_{C_3H_8} + 2\Phi_{C_6H_{14}} + \Phi_{C_3H_6})$, in isooctane

$\eta^S < 0.20$ in the vapor phase, while $\eta^T > 0.95$ and $\eta^S < 0.05$ in isooctane. However, for reasons which we are going to describe below, these results should be accepted with some reserve.

The results on the quenching of 4-heptanol and n-butanol formation in the vapor phase and in isooctane are given in Fig. 10 and 11, respectively. The corresponding
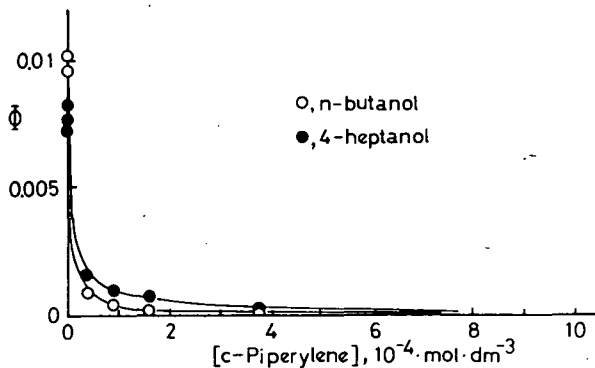

Fig. 10. Quenching of 4-heptanol and n-butanol formation by piperylene in the vapor phase. T=298 K, $[C_3H_7CHO]_0 = 2.7 \cdot 10^{-3}$ mol·dm^{-3}, $\lambda = 313$ nm, $I_0 = 6.5 \cdot 10^{-10}$ einstein·cm^{-2}·s^{-1}
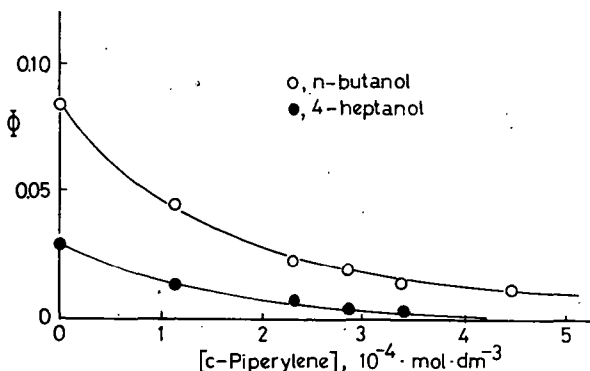

Fig. 11. Quenching of 4-heptanol and n-butanol formation by piperylene in isooctane. T=298 K, $[C_3H_7CHO] = 1 \cdot 10^{-2}$ mol·dm^{-3}, $\lambda = 313$ nm, $I_0 = 5 \cdot 10^{-9}$ einstein·cm^{-2}·s^{-1}

relative quenching plots of the characteristic product quantum yields (the sum of the quantum yields of 4-heptanol and n-butanol formation) are shown in Fig. 10 and 11. From these one may conclude that, under the conditions of our investigation, reaction IV occurs from the triplet state; *i.e.* $\eta^T \sim 1.0$ and $\eta^S \sim 0$ both in the vapor phase and in isooctane.

The excited singlet and triplet state contributions to primary reactions I, II, II′ and IV in *n*-butyraldehyde photolysis, obtained from piperylene quenching experiments, are summarized in Table IV. The results show the excited state precursor involved in reaction I and IV to be the triplet aldehyde molecule, while reactions II and II′ occur from both the excited singlet and the triplet states. The role of the triplet state is more important in isooctane than in the vapor phase.
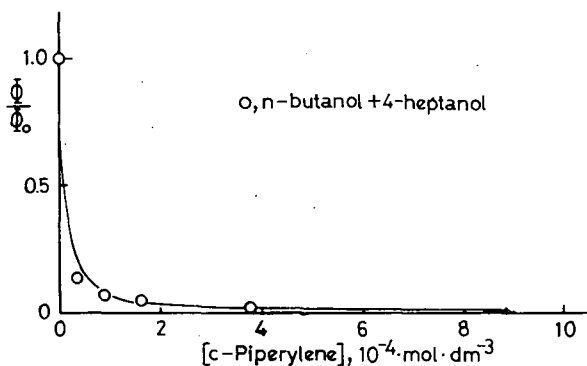

Fig. 12. Relative quenching plot of the characteristic product quantum yield for reaction IV in the vapor phase
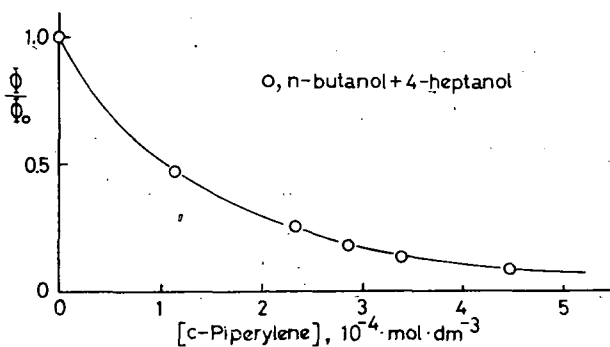

Fig. 13. Relative quenching plot of the characteristic product quantum yield for reaction IV in isooctane

The singlet state energy of *n*-butyraldehyde has been estimated by LEBOURGEOIS *et al.* [10], on the basis of the fluorescence and absorption spectra, to be about 86 kcal $\cdot$ mol^{-1}. The *n*-butyraldehyde quenches the triplet state of acetone [7] (for which a triplet energy of 80 kcal $\cdot$ mol^{-1} has been estimated [12]), on the other hand *cis*-butene-2 (with a triplet energy of about 78.8 kcal $\cdot$ mol^{-1} [13]) is an inefficient quencher of the triplet *n*-butyraldehyde [14]. From these data we estimated the lowest level of the triplet state of *n*-butyraldehyde to be about 78 kcal $\cdot$ mol^{-1} above the ground state.

Table IV

The role of the excited singlet and triplet states in primary reactions
I, II, II' and IV of n-butyraldehyde photolysis

	Reaction I	Reaction II	Reaction II'	Reaction IV
Vapor phase				
η^S	<0.20	0.55	0.20	~0
η^T	>0.80	0.45	0.80	~1.0
Solution				
η^S	<0.05	0.25	0.20	~0
η^T	>0.95	0.75	0.80	~1.0

The *cis*-piperylene has a low triplet state energy (which is about $56.9 \text{ kcal} \cdot \text{mol}^{-1}$ above the ground state [15]), thus very efficient triplet energy transfer is expected to occur from *n*-butyraldehyde to the conjugated olefin:

$$^3A + P \rightarrow A + {}^3P \qquad (3)$$

where A and ^3A stand for the ground state and triplet state of the aldehyde, while P and ^3P designate the ground state and triplet state of piperylene, respectively. In accordance with this supposition we found that low concentrations of piperylene ($10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ in the vapor phase and $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ in solution) quenched the decomposition of *n*-butyraldehyde. The quenching effect of piperylene is caused by energy transfer, which is indicated by the simultaneous occurrence of the *cis-trans* isomerization of the olefin. Thus, there is no doubt that efficient triplet energy transfer took place under the conditions used in our experiments, however, it has not been examined in this paper whether some singlet energy transfer also occurred at the highest piperylene concentrations. Experiments planned at even higher quencher concentrations — which are in progress in our laboratory — shall throw light on this question.

Only physical quenching caused by piperylene has been considered so far. However, free radicals formed in the primary processes might react with the conjugated olefin causing chemical quenching which could remain unrecognized. The observation [14] that the quantum yield of piperylene *cis-trans* isomerization was found to be similar but somewhat less than the value expected from the extent of decrease of product quantum yields seems to indicate that some trapping of the free radicals occurred. If this is so, the role of the triplet state in reaction I (and perhaps in reaction IV) could be somewhat less and that of the excited singlet state a little more important than indicated by the figures given in Table IV. Further experiments with triplet quenchers not reacting with free radicals are in progress and the results will be reported in another paper.

<p align="center">*   *   *</p>

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РОЛЬ ВОЗБУЖДЕННЫХ СОСТОЯНИЙ В ФОТОЛИЗЕ *н*-МАСЛЯНОГО АЛЬДЕГИДА, I.
Тушение триплетного состояния пипериленом

М. Тельдеши, Т. Берцеш и А. Нача

Описан экспериментальный метод пригодный для изучения роли возбужденных состояний в фотолизе *н*-масляного альдегида. Даны предварительные экспериментальные результаты полученные с применением в качестве тушителя пиперилена в газовой фазе и в растворе (растворитель изооктан) и оценены доли синглетного и триплетного состояний в четырех главных первичных фотохимических процессах фотолиза *н*-масляного альдегида при длине волны 313 нм.