PHOTOPOLYMERIZATION OF BENZALDEHYDE VAPOUR AT 366 nm

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(Received July 17, 1985)

Summary

The major product of the irradiation of benzaldehyde vapour at 366 nm and at 338 K and 353 K is a yellowish polymer. Trace quantities of CO, benzene and toluene are also formed. Under the initial conditions the rate of pressure decrease is first order with respect to the incident light intensity and about 1/2 order with respect to the benzaldehyde concentration. Although the quantum yields for benzaldehyde disappearance lie in the range 0.8 - 2.1, these correspond to quantum yields for photopolymer formation of only 0.07 - 0.17. Possible initiation mechanisms are discussed.

1. Introduction

The photochemical reactions of benzaldehyde depend strongly on the environment of the excited molecules and on the energy of the exciting photons. For example, the major products in solution are formed via ketyl and benzoyl radicals [1] whereas molecular decomposition to benzene and CO is the major process occurring upon irradiation of benzaldehyde vapour in the $\pi^* \leftarrow \pi$ absorption band at 276 nm [2, 3]. In sharp contrast, the major product of the irradiation of benzaldehyde vapour in the $\pi^* \leftarrow n$ absorption band is a yellowish polymer [3 - 6] which has been used as a convenient photosensitizer for cross-phase solid–gas photosensitizations [5, 6]. Although the photoinduced polymerization of pure benzaldehyde vapour was reported as early as 1933 [4], an investigation of the polymer's properties began only recently [5, 6]. In this paper we report some of the photochemical kinetic results obtained in our laboratory during our studies on the benzaldehyde photopolymer (BPOL) formed by irradiation of the monomer in the vapour phase at 366 nm.

2. Experimental details

The benzaldehyde was purified as described previously [7]. The photolyses were performed by passing collimated light beams through the plane

Pyrex windows of a cylindrical cell (internal diameter, 3.8 cm; length, 11.9 cm). The benzaldehyde pressure was monitored continuously by means of a Pyrex spoon gauge. The reaction system was enclosed in a box fitted with glass windows; the temperature in the box was regulated using rapid air circulation and a differential heating system coupled to a thermocouple monitor. The light intensities were determined by means of classical potassium ferrioxalate actinometry using $\Phi = 1.21$ [8]. For the experiments with $I_0 = 1.57 \times 10^{-8}$ einstein s^{-1} and 2.52×10^{-8} einstein s^{-1}, the light source was a Phillips HPK 125 W "Wood" blacklight lamp (mercury lines, $\lambda = 365.0$ - 366.3 nm). For $I_0 = 6.64 \times 10^{-8}$ einstein s^{-1}, a Phillips Philora HPK 125 medium pressure lamp was used. In this case visible light was removed from the beam before it entered the cell by using a filter from a UVSL black light lamp; a glass filter with a sharp cut-off at 320 nm was also used to absorb any light which could excite the benzaldehyde to its $\pi^*-\pi$ state. The procedures used to clean the cell and to test its "cleanliness" have been described previously [6].

3. Results and discussion

3.1. Minor products of the photolyses

As in the earlier photolyses of benzaldehyde in the $\pi^* \leftarrow n$ absorption band [3 - 6], polymerization is found to be the only major process accounting for the disappearance of the substrate from the vapour phase. Analysis of the residual gases after photolysis reveals trace quantities of CO, benzene and toluene in the benzaldehyde. The quantum yields of CO and benzene are estimated to be less than 10^{-4} whereas that of toluene is lower by a factor of 10. These results are compatible with those of Berger *et al.* [3] who found $\phi(C_6H_6) \approx 0.001$ and $\phi(CO) < 0.002$ for the photolysis of benzaldehyde at 365 nm and pressures from 39 to 372 mTorr. These minor products may be partly formed by secondary photolysis of the polymer. In any case they will not be considered below.

3.2. Effect of the presence of BPOL on the polymerization rate

Since BPOL is a known triplet energy donor, absorbing at 366 nm [6], it was suspected that it might play a role in the photopolymerization of the benzaldehyde. The effect of the presence of BPOL on the reaction rate v was examined by carrying out duplicate experiments (same temperature, pressure and light intensity), the first to about 50% completion in a clean cell, the second in the same cell after evacuation to 10^{-5} Torr for at least 24 h. Typical results are shown in Fig. 1. BPOL appears to have only a small retarding effect (less than 10%) on the rate of pressure decrease. This could be due to absorption of the incident light by BPOL and/or reflection at the polymer—cell interface.
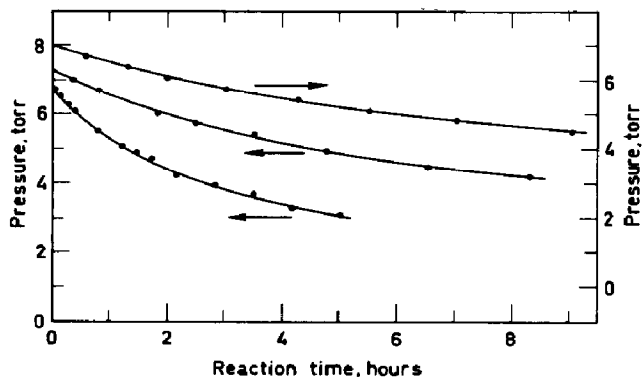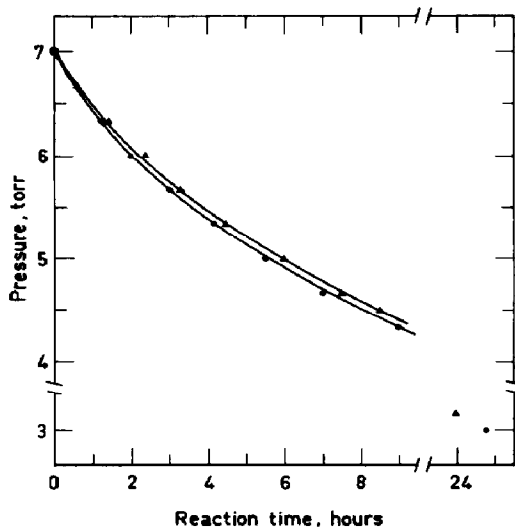
Fig. 1. Experiments performed under the same conditions of initial pressure, incident light intensity and temperature: ▲, in a clean cell; ●, in the same cell with the BPOL film deposited during the previous photopolymerization.

Fig. 2. Total pressure as a function of reaction time at 338 K: top curve, $I_0 = 1.57 \times 10^{-8}$ einstein s^{-1}; middle curve, $I_0 = 2.52 \times 10^{-8}$ einstein s^{-1}; bottom curve, $I_0 = 6.64 \times 10^{-8}$ einstein s^{-1}.

3.3. Dependence of the rate and quantum yields on the incident light intensity I_0

A series of experiments at 338 K and benzaldehyde pressure $P = 7.1 \pm 0.2$ Torr was carried out at I_0 values of 1.57, 2.52 and 6.64×10^{-8} einstein s^{-1} (Fig. 2). The initial rates v_0 of photopolymerization were determined from a least-squares treatment of plots of ln v versus ln P (see Fig. 3). For the v_0, the order with respect to I_0 is unity within experimental error. For each experiment, however, the rate of pressure decrease v_t during the course
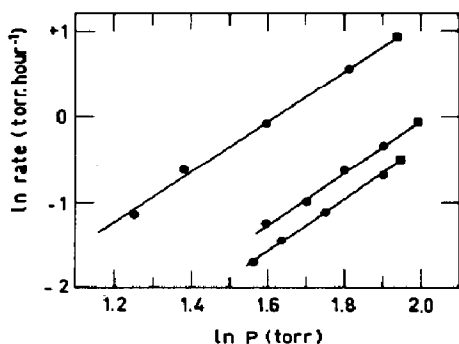

Fig. 3. Plots of ln v vs. ln P for experiments at 338 K: top curve, $I_0 = 6.64 \times 10^{-8}$ einstein s^{-1}; middle curve, $I_0 = 2.52 \times 10^{-8}$ einstein s^{-1}; bottom curve, $I_0 = 1.57 \times 10^{-8}$ einstein s^{-1}. ■, initial rates obtained from a least-squares treatment of the data.

of a reaction may be represented empirically by

$$v_t \propto I_0 P^m \tag{1}$$

where $m \approx 3$.

3.4. Effect of benzaldehyde pressure and of temperature on the rates

The results of experiments with $I_0 = 1.57 \times 10^{-8}$ einstein s^{-1} and benzaldehyde pressures ranging from 3.0 to 9.6 Torr at 338 K and from 3.0 to 20.1 Torr at 353 K are given in Figs. 4 and 5. (Results of experiments at 353 K and $I_0 = 6.64 \times 10^{-8}$ einstein s^{-1} are also given in Fig. 5 for comparison.) To avoid unwanted condensation in the reaction system, the highest benzaldehyde pressure used at each temperature is about 80% of the vapour pressure. (Benzaldehyde has vapour pressures of 12.2 Torr and 24.9 Torr at 338 K and 353 K respectively [9].) From the plots of $\ln v$ versus $\ln P$ in Fig. 5, it is clear that at both temperatures, for a given pressure, v_0 is much higher than v_t obtained during the course of a reaction. There must therefore be some inhibiting (or reverse) process occurring in the photopolymerization.

At both temperatures v_0 is given empirically by

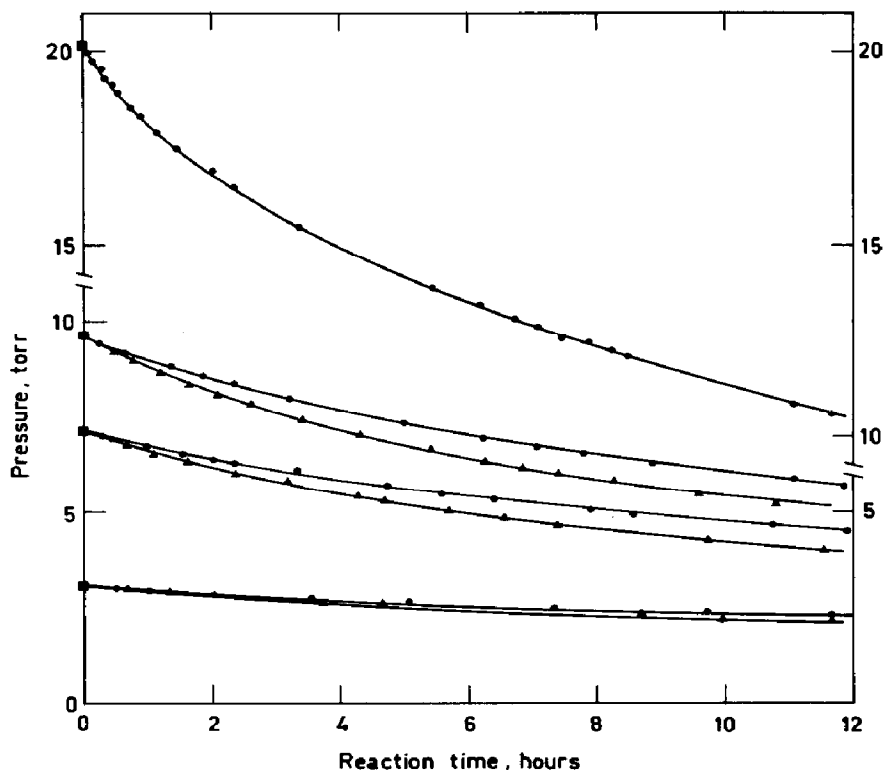$$v_0 \propto I_0 P^n \tag{2}$$

Fig. 4. Dependence of the total pressure on the reaction time with $I_0 = 1.57 \times 10^{-8}$ einstein s^{-1}: ●, 353 K; ▲, 338 K.
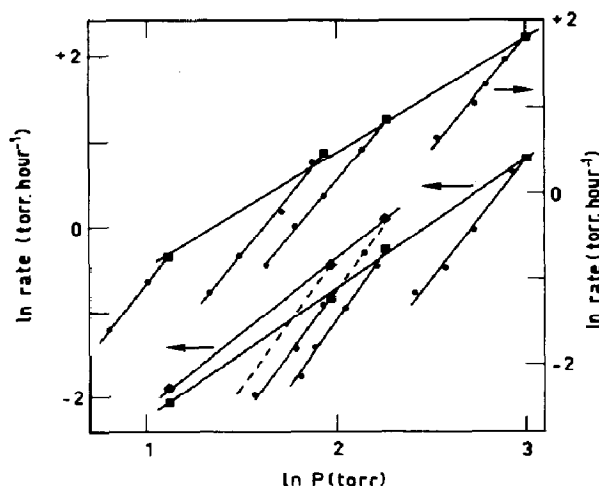
Fig. 5. Plot of $\ln v$ *vs.* $\ln P$: ◆ and ■, extrapolated initial rates at 338 K and 353 K respectively. Upper group, $I_0 = 6.64 \times 10^{-8}$ einstein s^{-1}; lower groups, $I_0 = 1.57 \times 10^{-8}$ einstein s^{-1}.

where a least-squares treatment yields $n = 1.7 \pm 0.1$ and $n = 1.4 \pm 0.1$ at 338 K and 353 K respectively. For benzaldehyde, the absorbed light intensity I_a under these conditions is nearly proportional to $I_0 P$ [10] (at 20 Torr the imprecision introduced by this approximation is about 7%) so that $v_0 \propto I_a P^{0.5}$ within experimental error.

For the v_t the average value of m (eqn. (1)) is just over 3 at 338 K whereas it is just under 3 at 353 K. The increase in temperature decreases the initial rate (at least at the higher pressures, see below) but produces a higher relative rate during the course of the reaction.

The rates at different temperatures should be compared at the same concentrations rather than at the same pressures. Plots of v_0 *versus* ln[benzaldehyde] were made for the above experiments as well as for some carried out at 338 K and 353 K with $I_0 = 1.57 \times 10^{-8}$ einstein s^{-1}. At the lowest concentrations (corresponding to 3 Torr), and for a given I_0, the rate observed at 353 K falls on the 338 K plot; at the concentrations corresponding to 9.6 Torr, v_0 at 338 K is 40% - 50% higher than that at 353 K. These results can be explained by a reverse step (depolymerization) which is favoured by the temperature increase and occurs from an excited species which may be collisionally stabilized.

3.5. Quantum yields of benzaldehyde consumption

The quantum yields for benzaldehyde disappearance under initial conditions ($\phi(-\text{B}) = v_0/I_a$) are quite high (see Fig. 6). $\phi(-\text{B})$ apparently increases towards a limiting value, which is temperature dependent, as the benzaldehyde concentration is increased. We previously determined $\phi(-\text{B}) = 1.7$ for $P = 5$ Torr at 323 K [6]. Berger *et al.* [3] found 0.36, 0.41 and 0.43 for the quantum yield of benzaldehyde consumption at P values of 39 mTorr, 175 mTorr and 372 mTorr respectively in the photolysis at 365 nm
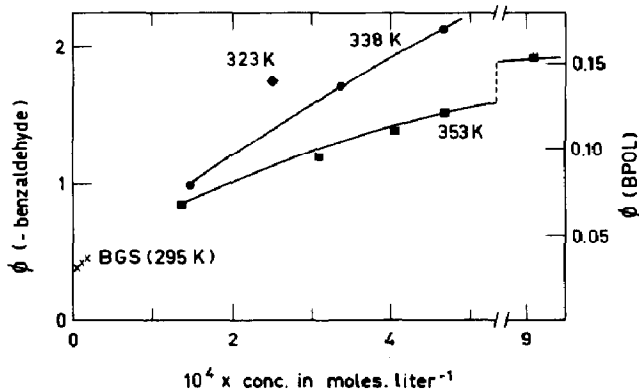
Fig. 6. Quantum yields of benzaldehyde consumption and BPOL formation under initial conditions at 323 K (♦, from ref. 6), 338 K (●) and 353 (■). ×, values reported by Berger *et al.* [3] for benzaldehyde disappearance at 295 K.

and 295 K. These values are also plotted in Fig. 6. The nearly constant values found by Berger *et al.* [3] do not fit an empirical equation such as eqn. (2) unless n is nearly unity. This is not consistent with our observation that n is higher at 338 K than at 353 K.

3.6. Mechanistic considerations

We have attempted several times to derive a mechanism for the photopolymerization of benzaldehyde. Each time the initiation was considered to occur via the reversible addition of a triplet (T_1) to a ground state molecule to give an activated species which simply adds another benzaldehyde molecule, and so on. However, Berger *et al.* [3] concluded that in the $\pi^* \leftarrow n$ photolysis "the benzaldehyde consuming process(es) is probably initiated either by radicals originating in S_1 or from a surface initiated reaction". Brühlmann and Huber [11], in a footnote, state that their "preliminary photochemical results for benzaldehyde indicate that decomposition following excitation into the $S_1(n\pi^*)$ state appears to be a surface-initiated reaction". We shall now consider these different possibilities.

3.6.1. Heterogeneous versus homogeneous initiation reactions

The above conclusions of Berger *et al.* [3] are based on the observation that addition of a triplet scavenger such as 2,3-diazabicyclo[2.2.1]hep-2-ene (DBH) did not affect the benzaldehyde consumption. In sharp contrast, we have found that the addition of 1,3-pentadiene inhibits the pressure-drop characteristic of BPOL formation completely, within experimental error. Also, a heterogeneous initiation mechanism would lead to a build-up of BPOL deposits primarily at the points where the light enters and exits the reaction cell. Instead it is distributed uniformly over the entire surface suggesting initiation in the homogeneous vapour phase and subsequent migration to the walls. Perhaps the major mechanism (and product?) of the polymerization is not the same in the photolyses in the torr and the millitorr pressure ranges.

3.6.2. Triplet versus excited electronic singlet (S₁) initiation

Competition between $S_1 \rightarrow T_1$ intersystem crossing and collision of the molecule in the S_1 state with a ground state benzaldehyde molecule to form a BPOL precursor should probably be excluded: the intersystem crossing rate has been estimated to be about 10^{12} s^{-1} [12]. Thus, for S_1 initiation of the photopolymerization to occur the quantum yield ϕ_{ISC} for intersystem crossing would have to be less than unity, the value deduced in our laboratory using benzaldehyde as a photosensitizer in the vapour phase [13]. Berger et al. [3] had questioned our value for ϕ_{ISC} and proposed $\phi_{ISC} = 0.85$, equal to the quantum yield of benzaldehyde-photosensitized DBH decomposition that they had obtained at 365 nm. This value appears to be too low, however; recent measurements by Brühlmann et al. [14], based on the benzaldehyde-photosensitized phosphorescence of biacetyl using excitation at 28 500 cm^{-1} (351 nm), give $\phi_{ISC} = 1.0 \pm 0.05$. They found that the phosphorescent excitation spectrum of benzaldehyde follows its $S_1 \leftarrow S_0$ absorption band until around 32 000 cm^{-1} (313 nm) and conclude that ϕ_{ISC} is independent of the S_1 excitation energy up to this point. Itoh et al. [15] also observed that the phosphorescence yield of benzaldehyde was constant in its $\pi^* \leftarrow$ n absorption band. The S_1 state is thus not a likely candidate for the initiation of BPOL formation since $\phi_{ISC} + \phi_{BPOL}$ would be greater than unity.

3.6.3. Triplet versus vibrationally excited ground state (S₀ᵛ) initiation

One cannot exclude the possibility that BPOL formation is initiated in a collision between a vibrationally excited ground state molecule and a thermalized molecule, following $T_1 \rightarrow S_0^v$ intersystem crossing. The reaction of the vibrationally excited ground state molecules eventually can be inhibited by the addition of an inert gas such as CO_2 which has no effect on the triplet energy transfer to added olefins [16]. Unfortunately no experiments were carried out with CO_2 and benzaldehyde alone. Nevertheless, it is more probable that the initiation occurs during a collision between molecules in the T_1 and S_0 states since their dipole moments are quite different [11]. This difference in dipole moments has been invoked as a possible reason for the important self-quenching of benzaldehyde phosphorescence ($k_{SQ} = 2.4 \times 10^4$ s^{-1} Torr^{-1} [11]). Combining the value for k_{SQ} with the collision-free lifetime of T_1 (2.3 ms [11]) one finds that self-quenching accounts for more than 99% of the T_1 decay even at the lowest benzaldehyde pressure used in this study. Since the quantum yields for BPOL formation lie in the range 0.07 - 0.17, only 7% - 17% of the self-quenching leads to the formation of BPOL.

3.7. Photopolymerization rates

The difference in the rates v_0 and v_t (see Section 3.4.), measured at identical pressures, temperatures and light intensities, is very puzzling. Except for the very minor products CO, benzene and toluene, no products other than BPOL are formed. The presence of proportionally larger quantities of BPOL on the walls from a previous reaction only decreases the rate

by a few percent. Another puzzling observation is that the average BPOL molecule contains 12 monomers. Nevertheless, a similar observation by Galego and Gandini [17] in the photopolymerization of liquid 2-furaldehyde shows that the polymer has an average molecular weight of 500 ± 50 or that it contains only 5 monomer units. For benzaldehyde, possible explanations would be (i) that the structure containing 12 monomer molecules is particularly photostable and (ii) that BPOL and all its precursors absorb light and undergo decomposition by loss of monomer units until BPOL is safely deposited on the walls.

4. Conclusions

The photopolymerization of benzaldehyde induced by absorption at 366 nm ($\pi^* \leftarrow n$) is an inefficient process with less than 20% of the excited molecules leading to polymer formation. The quantum yield of benzaldehyde disappearance is high, however, increasing from 0.8 to 2.1 as the pressure is increased from 3 Torr to 20 Torr at 353 K. The mechanism most probably involves initiation via the addition of a triplet to a ground state benzaldehyde molecule. The mechanism for benzaldehyde disappearance for photolysis in the $\pi^* \leftarrow n$ region and at pressures in the millitorr range may be different from that leading to BPOL formation at a pressure of 3 Torr or above.

Acknowledgment

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