PHOTOCLEAVAGE OF BENZIL

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Summary

The photolysis of benzil in n-dodecane was studied in the 140 - 180 °C temperature range. The carbonyl–carbonyl photocleavage yield increases from 2.5×10^{-3} at 140 °C to 6×10^{-3} at 180 °C. From these yields and from the triplet lifetimes obtained from quenching experiments employing diethylhydroxylamine as the selective triplet quencher, it is concluded that the rate constant for the process

$$^3\text{benzil} \longrightarrow 2\text{C}_6\text{H}_5\text{CO}\cdot$$
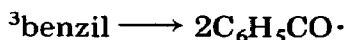
is 4.6×10^4 s^{-1} at 160 °C. This low photocleavage rate is due to a large (about 17 kcal mol^{-1}) activation energy.

1. Introduction

The photolysis of benzil has attracted much attention but there have been no determinations of the photocleavage yields or of the photocleavage rate constants. Carbonyl–carbonyl photocleavage leading to a benzoyl radical pair has been proposed as a significant reaction pathway [1], but this claim has been questioned [2]. Similarly, the behaviour of benzil as a photo-initiator of free-radical vinyl polymerization, although previously explained in terms of a type I photocleavage reaction [3], has recently been attributed to photoreduction by or addition to the monomer [4]. This lack of photofragmentation has been rationalized in terms of the endothermicity of the process and its symmetry-forbidden character [5]. In contrast, the reverse reaction, benzoyl radical combination to produce triplet benzil, seems to be a relatively efficient process [6, 7]. To obtain a more complete understanding of these processes we have studied the photolysis of benzil under conditions such as to maximize the photocleavage yield.

2. Experimental details

Benzil (Hopkins and Williams) was recrystallized twice from ethanol. n-Dodecane (Merck) was employed as received. Diethylhydroxylamine

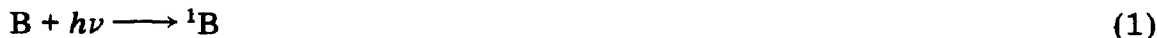(DEHA), an Ethyl Corporation product, was distilled under vacuum before use.

Conventional photolyses were carried out with light of 366 nm obtained from a medium pressure mercury lamp and glass filters. Constant temperatures (±0.5 °C) up to 180 °C were obtained by introducing a small merry-go-round into a double-walled reservoir heated by refluxing liquids at controlled pressures. Actinometry was performed employing valerophenone in n-dodecane as the reference. For this compound, the acetophenone quantum yield was taken as 0.33 over the temperature range considered [8]. Product analyses were carried out by gas–liquid chromatography. The benzil concentration was about 0.03 M, and the absorbed light intensity was around 2.5×10^{16} quanta ml^{-1} s^{-1}. No product formation was detected in the dark runs.

The triplet lifetimes were measured with the laser facilities of the National Research Council of Canada [9] by monitoring the transient decay at 490 nm.

3. Results and discussion

The photolysis of benzil B at high temperatures (140 - 180 °C) in n-dodecane gives benzaldehyde as the main photofragmentation product. In particular, it is relevant to note that the benzene yields are less than 10% of the benzaldehyde yields.

The yield of benzaldehyde is modified by DEHA addition. At low DEHA concentrations, the yield increases (up to 1.2 times that obtained without DEHA) with increases in the DEHA concentration. At DEHA concentrations greater than 10^{-3} M, the benzaldehyde yield markedly decreases when the additive concentration increases. The reaction scheme proposed to interpret the results is as follows:

$$B + h\nu \longrightarrow {}^1B \tag{1}$$

$$^1B \longrightarrow {}^3B \tag{2}$$

$$^3B \longrightarrow 2C_6H_5CO\cdot \tag{3}$$

$$^3B(+RH) \longrightarrow deactivation \tag{4}$$

$$^3B + DEHA \longrightarrow deactivation \tag{5}$$

$$2C_6H_5CO\cdot \longrightarrow B \tag{6}$$

$$C_6H_5CO\cdot + RH \longrightarrow C_6H_5COH + R\cdot \tag{7}$$

$$C_6H_5CO\cdot + DEHA \longrightarrow C_6H_5COH + (C_2H_5)_2NO\cdot \tag{8}$$

The effect of DEHA can be understood in terms of reactions (5) and (8). At low DEHA concentrations, the occurrence of reaction (8) increases the yield of benzaldehyde. At higher DEHA concentrations, deactivation of triplet benzil by reaction (5) decreases the yield. In particular, the significant

decrease in the benzaldehyde yield observed at DEHA concentrations of the order of 10^{-3} M suggests that singlet quenching is not significant because of the short lifetime (2.1 ns [10]) of this state. Furthermore, the low benzene yield implies that the only significant photocleavage breaks the central carbonyl–carbonyl bond.

The reaction scheme comprising reactions (1) - (8) implies that, at high DEHA concentrations, the photocleavage yield can be equated to one-half the benzaldehyde yield. The photocleavage yield ϕ^0 in the absence of DEHA was obtained by extrapolating at zero DEHA concentration the data obtained at DEHA concentrations greater than 0.5 mM. The photocleavage yields obtained by this procedure are given in Fig. 1 and ranged from 2.5×10^{-3} at 140 °C to 6×10^{-3} at 180 °C. The apparent activation energy of the photocleavage is nearly 7.4 kcal mol^{-1}.
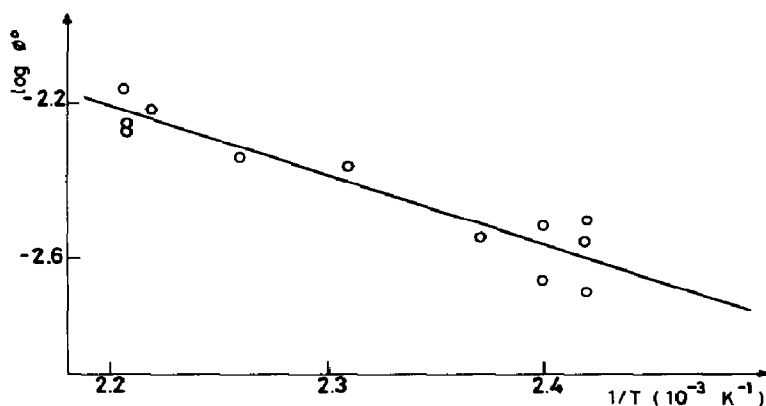

Fig. 1. Dependence of the photocleavage yield on temperature.

The values of k_3 can be obtained from ϕ^0 and the triplet lifetimes. The triplet lifetimes were derived from Stern–Volmer plots employing DEHA as the quencher. The plots obtained at 140 and 180 °C are given in Fig. 2. The value of τ^0 was then obtained from

$$\tau^0 = \frac{K_{SV}}{k_Q}$$

where K_{SV} is the slope of the Stern–Volmer plot and k_Q is the quenching rate constant. These values were obtained by extrapolation of k_Q values measured at lower temperatures. This procedure was considered to be more reliable than extrapolation of the triplet lifetimes because of the possibility of changes in the reactions controlling the triplet lifetimes at low temperatures (up to 60 °C) and at the temperatures at which the photocleavage was measured [11]. (Absolute lifetimes could only be determined up to 60 °C.)

The values of k_Q were evaluated by measuring the decay of triplet benzil at different DEHA concentrations in the 0 - 60 °C temperature range. The k_Q values obtained are plotted according to the Arrhenius equation in Fig. 3. From this figure
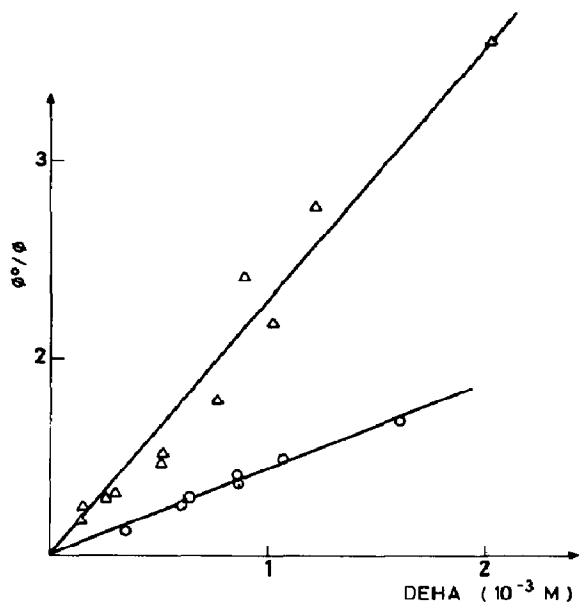
112

Fig. 2. Stern–Volmer plots for the benzaldehyde yield as a function of the DEHA concentration (the data were obtained at DEHA concentrations high enough to ensure that all the $C_6H_5CO\cdot$ radicals were trapped): $\triangle$, 140 °C; $\bigcirc$, 180 °C.

$$\log\{k_Q(\mathrm{M^{-1}\,s^{-1}})\} = 11.2 - \frac{2.7}{2.3RT}$$

Both the A value and the activation energy measured are compatible with a diffusion-controlled process [12, 13]. In particular, it is interesting to note that for the recombination of *tert*-butyl radicals in *n*-dodecane Schuh
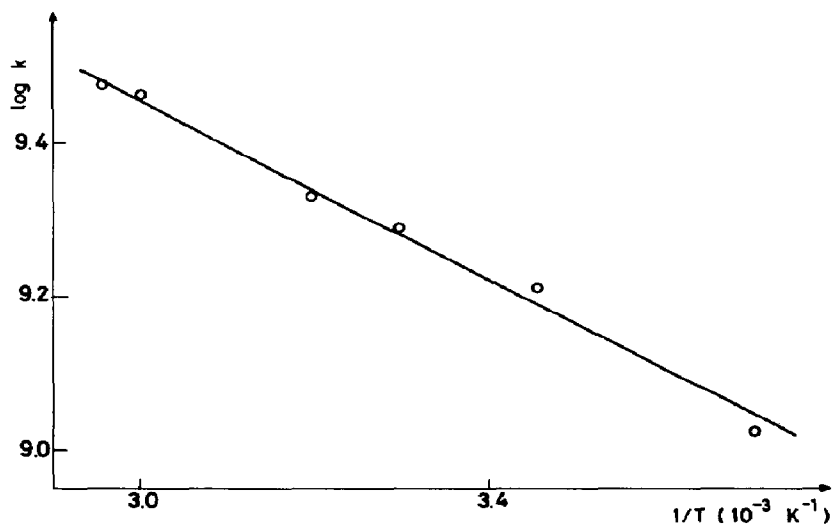

Fig. 3. Temperature dependence of the DEHA quenching rate constant.

and Fischer [13] found an activation energy of 2.71 ± 0.04 kcal mol^{-1} for the diffusion-controlled process.

Quenching of excited carbonyls by DEHA involves hydrogen abstraction from the labile O—H bond [14]. The same process takes place in the quenching of benzil triplets, as evidenced by the formation of

$$C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{\underset{.}{C}}-C_6H_5$$
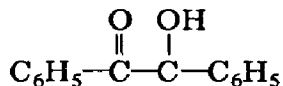
radicals. If the hydrogen transfer step does not control the rate of the quenching process at low temperatures, its activation energy must be even lower than that associated with the diffusion and it cannot became rate controlling at higher temperatures. This implies that the Arrhenius parameters measured for the quenching process in the 0 - 60 °C temperature range can be extrapolated to higher temperatures (assumption of a different law for the change in k_Q with temperature does not appreciably modify the extrapolated values). From a combination of these values with the ϕ^0 and $k_Q\tau^0$ values measured in the 140 - 180 °C range the rate constant for photocleavage (process (3)) is calculated to be 4.6×10^4 s^{-1} at 160 °C and it is found that the process takes place with an activation energy of about 17 ± 3 kcal mol^{-1} with a pre-exponential A factor of nearly 10^{15} s^{-1} (Fig. 4).

The considerably larger activation energy obtained for reaction (3) compared with that measured for the apparent activation energy of the photocleavage (7.4 kcal mol^{-1} from the photocleavage quantum yield) implies that the main process determining the triplet lifetimes has a significant activation energy. The most probable process determining the triplet
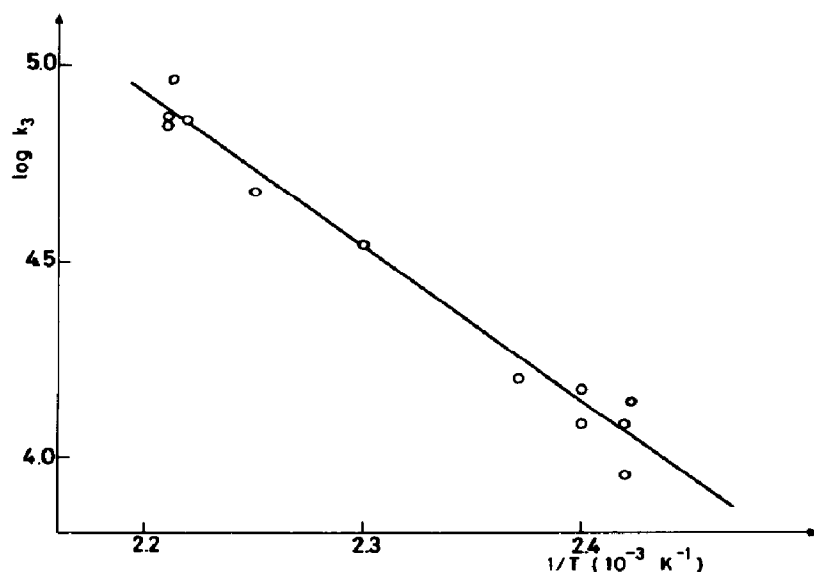

Fig. 4. Arrhenius plot for the photocleavage rate constant.

lifetimes at the high temperatures considered is photoreduction of the excited molecule by the solvent.

The activation energy obtained is larger than the estimated endothermicity of the process (10.3 kcal mol^{-1}) [5]. Nevertheless, it must be taken into account that the uncertainty in this value was considered to be as large as 6 kcal mol^{-1}. The relevant point is that the low rate of the photocleavage is mainly due to its activation energy and this mainly arises from the endothermicity of the process. From the luminescence observed in the electrolysis of phenylglyoxylic acid partially neutralized in acetonitrile, de la Fuente *et al.* [7] estimated that the rate constant for the reverse reaction, *i.e.* benzoyl recombination to triplet benzil, takes place with a rate constant of the order of 10^7 M^{-1} s^{-1}. This large value also implies that the photocleavage energy barrier is mainly determined by the endothermicity of the process. Unfortunately, the lack of reliable thermochemical data, as well as the large errors involved in extrapolation of the present results to room temperature and in the evaluation of the rate constant for benzoyl recombination to produce the benzil triplet, does not allow a quantitative comparison of both sets of data.

Acknowledgments

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