

FLASH PHOTOLYSIS OF BENZILS

GOUR KRISHNA DAS MOHAPATRA, JAYA BHATTACHARYA, JIBANDHAN BANDOPADHYAY and SUBHASH CHANDRA BERA

Department of Chemistry, Jadavpur University, Calcutta 700032 (India)

(Received March 9, 1987)

Summary

Flash photolytic studies on benzils are reported. Two different geometrical conformers, one puckered and the other planar, have been characterized for triplet benzils and benzil anions. They are produced under different conditions. The puckered benzil triplet formed in ethanol glass at 77 K shows an absorption peak at 490 nm accompanied by vibrational bands at 1600 and 1000 cm^{-1} . The planar benzil triplet, which appears at room temperature, absorbs at 470 nm.

Two different conformers of the benzil anion are also found to be present in two different solvents, ethanol and acetonitrile. The planar form absorbs at 540 nm in ethanol and the puckered form absorbs at 620 nm in acetonitrile. Mesityl and α -furyl do not undergo a change in conformation under similar conditions.

1. Introduction

The photophysics and photochemistry of benzil ($\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_5$) are interesting as a result of the compound's ability to change conformation either in the ground or in the excited state. The molecule is puckered in the ground state (the angle between the planes of the two halves is 72°) [1]. It can be made planar in a crystal of *trans*-stilbene molecules [2] or by doping it in a matrix of methylcyclohexane [3]. The conformation changes in the excited state have been studied mostly from its emission properties [4 - 8]. The conformation change has been substantiated from studies such as ENDOR [9], CIDEP [10] and dipole moments [11]. There have been several studies of triplet-triplet absorption, hydrogen adduct formation and radical ion formation, but so far no attempt has been made to explore the conformation change either in the triplet state or in the radical or radical anionic state. Flash photolytic studies on benzil were started as early as 1958 by Porter and Windsor [12]. They reported the triplet-triplet absorption and the formation of a hydrogen adduct radical in hydrogen-bonding solvents. They showed that the neutral hydrogen adduct radical can dissociate to the

radical anion and remain in equilibrium [13]. Later on, the techniques of laser flash photolysis [14, 15] and γ -ray radiolysis [16] were employed to study the hydrogen adduct radical and the radical anion of benzil. The aim of the present study has been to explore the possibility of conformation change in the triplet, radical and radical anion states of benzil.

2. Experimental details

The flash kinetics apparatus (model K-2) in this work was supplied by Applied Photophysics, London. In this set-up, a capacitor of $1 \mu\text{F}$ is charged up to 20 kV and discharged in the flash cavity through two xenon flash-lamps 100 mm long and 5 mm in diameter. The monitoring source is a 100 W tungsten-halogen lamp. The cylindrical sample cell is 100 mm long and 15 mm in diameter. The signal from an IP 28 photomultiplier working under five-stage amplification and an anode load resistance of 560Ω is fed to a Tektronix storage oscilloscope DM 64. The data are directly read from the oscilloscope screen. Throughout the study, we used a flash-lamp voltage of 15 kV. The uranyl oxalate actinometer estimates 5.5×10^{17} photons per flash at the flash-lamp voltage of 15 kV. The low temperature flash excitation spectra were recorded using a special attachment to the set-up, consisting of a quartz Dewar and cells (models 1481 and 1482).

The limitation of this set-up is obviously its long time constant. In the wavelength region below 390 nm, where benzil absorbs and the monitoring light intensity falls, the monitoring photomultiplier voltage has to be set relatively high and in consequence the exciting light interferes more with the flash-excited absorption. Thus, below 390 nm, data are unreliable at times shorter than $25 \mu\text{s}$ and discarded. However, in the higher wavelength region, the interference is small and data taken above $20 \mu\text{s}$ are reliable. One plus point of this set-up is its 100 mm long sample cell which is convenient to work with at relatively lower reagent concentrations. The reduction potentials are measured with respect to a saturated calomel electrode in the deaerated condition with a standard potentiostat Wenking ST 72 associated with a voltage scan generator model SG 72 and a Houston omnigraphic x - y recorder. Emission studies are carried out using a Perkin-Elmer fluorimeter (model MPF 44B).

Benzil (E. Merck) was used after recrystallization from ethanol. The 4,4'-dimethylbenzil [17], 4,4'-dimethoxybenzil [17], 4,4'-dichlorobenzil [18], 2,2'-dichlorobenzil [19] and α -fural [17, 20] were prepared using standard methods of oxidation from the respective benzoin. The benzoin were in turn obtained by benzoin condensation of the respective benzaldehydes. Mesital [21] (2,2',4,4',6,6'-hexamethylbenzil) and *o*-tolil [22] (2,2'-dimethylbenzil) were prepared by Grignard reactions of the respective acid chlorides. Finally, all the derivatives of benzil and α -fural were recrystallized from ethanol before use.

All solvents, ethanol, benzene and acetonitrile were purified following standard methods [23]. Triethylamine was distilled over potassium hydroxide.

The solutions were deoxygenated before use by passing dry nitrogen through for about 1 h. The reproducibility of the results was checked frequently and compared with those obtained from solutions which had undergone freeze-pump-thaw cycles.

3. Results and discussion

The phosphorescence of benzil in ethanol glass at 77 K appears at 520 nm (Fig. 1). The phosphorescence of benzil from benzil crystal is the same as that from ethanol glass and originates from the puckered triplet conformation of the molecule. The triplet geometry of the molecule in the crystal has been determined from ENDOR studies [9]. It is very likely that the molecule will retain its normal puckered geometry in a rigid environment. Hence the triplet-triplet absorption of benzil (Fig. 2) at 77 K originates from its puckered conformation. The absorption maximum appears at 490 nm with a few vibrational bands. The spacings of 1600 ± 50 and $1000 \pm$

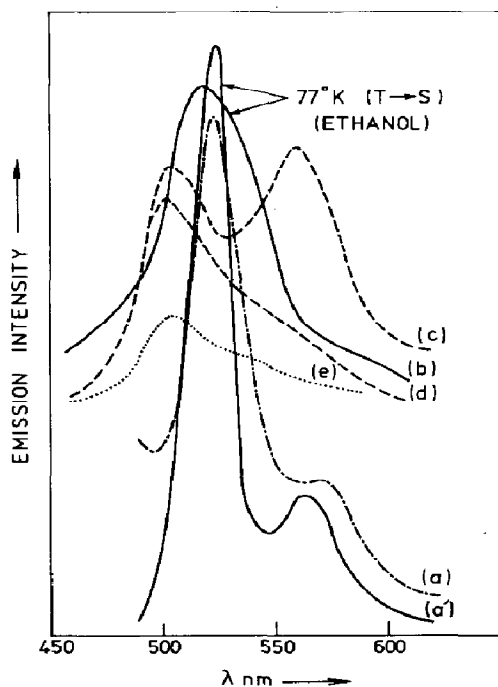


Fig. 1. Emission spectra of benzil and α -furil in the concentration range 1.0×10^{-4} - 5.0×10^{-4} M: curve a', α -furil in ethanol at 77 K; curve b, benzil in ethanol at 77 K; curve a, α -furil in deoxygenated benzene at room temperature; curve c, benzil in deoxygenated benzene at room temperature; curve d, benzil in benzene in the presence of air at room temperature; curve e, benzil in benzene in the presence of 6.0×10^{-2} M triethylamine at room temperature.

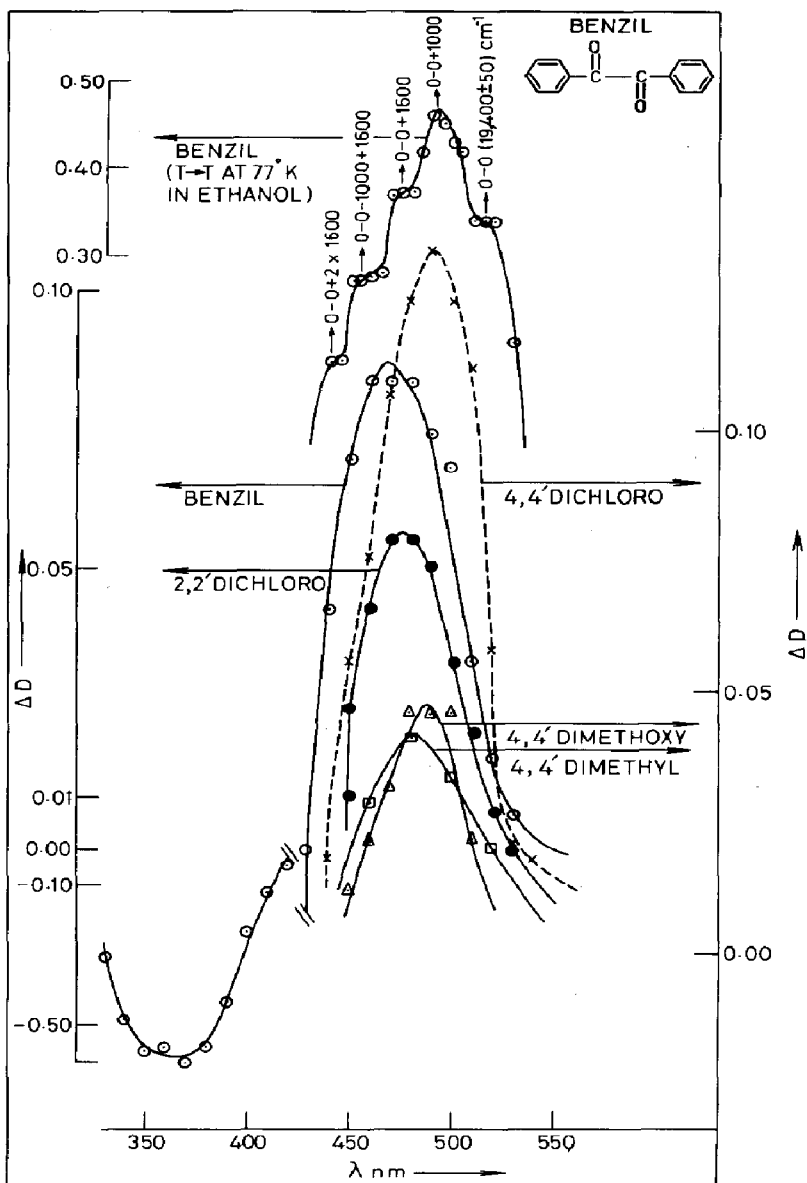


Fig. 2. Triplet-triplet absorption of benzil and its derivatives (2.0×10^{-3} M) at room temperature in benzene and at 77 K in ethanol (benzil, 1.0×10^{-4} M).

50 cm^{-1} are prominent in the spectra. The $1600 \pm 50 \text{ cm}^{-1}$ spacing compares well with C=O stretching and the $1000 \pm 50 \text{ cm}^{-1}$ spacing might be associated with the central $-\text{CO}-\text{CO}-$ stretching. The kinetics of the 490 nm flash absorption and 520 nm emission are the same with a lifetime of about 4 ms [24].

The emission of benzil changes from green (520 nm) to yellow (565 nm) as the glass softens with increasing temperature. At room temperature the emission appears at 505 and 565 nm in deoxygenated hydrocarbon solu-

tions [6]. In Fig. 1, emissions of benzil in benzene are shown. A similar emission spectrum appears in acetonitrile medium. Of the two bands, the 505 nm emission is fluorescence and the 565 nm emission is phosphorescence. The phosphorescent nature of the 565 nm emission has been confirmed from its lifetime [7, 24]. The geometry of the 565 nm emitting state is planar which has been confirmed from various studies such as CIDEP [10] and dipole moments [11].

The emission of α -furyl in ethanol glass at 77 K and in benzene at room temperature is shown in Fig. 1. This emission does not change or shift in going from rigid to fluid medium, which is in sharp contrast with that of benzil. Also the dipole moment of the α -furyl triplet in benzene is not zero [11], which is in contrast with that of benzil. Therefore the puckered conformation of α -furyl remains unaltered in going from rigid glass to fluid medium. The triplet-triplet absorption of benzil in benzene at room temperature appears at 470 nm (Fig. 2) while in acetonitrile it appears at 480 nm and is also present at a time of 25 μ s in the time-resolved spectra of the benzil-triethylamine system (see Fig. 5). It is interesting to note that the conformation change results in a large red shift both in the ground state absorption [4] and in the phosphorescence spectra [5 - 8] but only a small shift in the triplet-triplet absorption as it appears for puckered benzil at 490 nm in ethanol glass and for planar benzil at 470 nm in benzene and at 480 nm in acetonitrile. The other derivatives of benzil show their triplet-triplet absorption in the region 470 - 490 nm (Fig. 2). In the triplet-triplet absorption, there is a bleaching in the region 360 - 410 nm due to strong ground state absorption in this region. The triplet decays are found to follow first-order decay kinetics and their lifetimes are given in Table 1. The second-order kinetics due to triplet-triplet quenching are not significant. This may be due to the low concentration of triplet produced under our experimental conditions.

The long time constant of the instrument does not permit us to record the triplet-triplet absorption of mesityl (2,2',4,4',6,6'-hexamethylbenzil) or α -furyl.

Benzil and its derivatives produce hydrogen adduct radicals from their respective triplets. On flash excitation in ethanol, the triplets are converted to the hydrogen adduct radical by abstracting hydrogen from ethanol. The hydrogen adduct radical of benzil can be produced in the presence of a hydrogen donor such as triethylamine. In the presence of triethylamine in benzene it forms the hydrogen adduct radical of benzil. With insufficient triethylamine (10^{-5} M, or less) benzil triplets are not completely quenched as found from the decay of the 490 nm absorption which consists of a faster decay of triplets followed by a slower decay due to radicals. The quenching of the benzil triplet has also been evidenced from the phosphorescence quenching by triethylamine (Fig. 1).

The absorption of the hydrogen adduct radical of benzil appears at 370 nm and 490 nm. The 370 nm band is strong and the 490 nm band is weak and broad. From pulse radiolysis the molar extinction coefficients of

TABLE 1

Compound	Triplet-triplet λ_{\max} in benzene (nm)	Triplet lifetime in benzene (μ s)	Hydrogen radical λ_{\max} in ethanol (nm)	Hydrogen radical decay in ethanol, $K_2 \times 10^{-4} \epsilon^{-1}$ (mol s)	Hydrogen radical λ_{\max} in ethanol (nm)	Radical anion decay in ethanol, $K_2 \times 10^{-4} \epsilon^{-1}$ (mol s)	Anion lifetime in ethanol (s)	Radical λ_{\max} in acetonitrile (nm)	Radical anion decay in acetonitrile, $K_2 \times 10^{-4} \epsilon^{-1}$ (mol s)	Reduction potential in acetonitrile (V)
Benzil	490 ^a 470	4.0 ms ^a 21.0	370; 500	6.7	370; 540	0.024	—	370; 620	0.40	-0.885
Mesitil	—	—	390	1.2	400	0.61	—	400; 430	0.87	—
2,2'-Dichloro-benzil	475	20.0	355; 410	2.5	350; 460	—	0.33	350; 510	0.078	-0.720
2,2'-Dimethyl-benzil	—	—	400; 500	5.5	—	—	—	—	—	—
4,4'-Dichloro-benzil	490	16.0	380; 500	6.7	360; 560	—	0.41	360; 640	0.053	-0.745
4,4'-Dimethoxy-benzil	490	21.0	410; 510	4.7	390; 530	0.05	—	380; 580	2.30	-0.995
4,4'-Dimethyl-benzil	480	17.0	380; 510	1.7	370; 540	0.47	—	—	—	-0.910
α -Furil	—	—	—	—	410; 620	0.002	—	390; 620	1.0	-0.700

^a In ethanol glass at 77 K. 2.0×10^{-3} M benzils are used in benzene for triplet decays at room temperature and 1.0×10^{-4} M benzil in ethanol at 77 K. $(0.5 - 1.0) \times 10^{-3}$ M benzils are used for the hydrogen radical in ethanol and 1.0×10^{-3} M benzils and 1.0×10^{-2} M triethylamine are used for radical anions in ethanol and acetonitrile. The radical anions of the chloro derivatives in ethanol follow first-order decay kinetics.

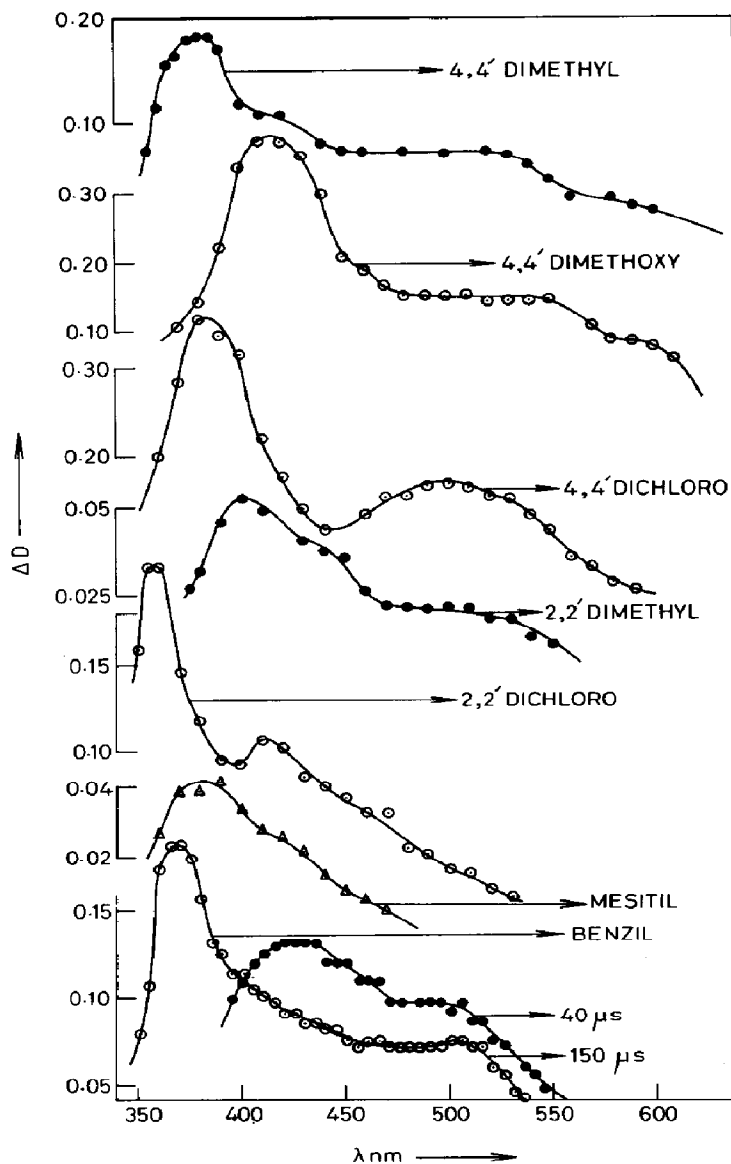


Fig. 3. Absorption spectra of hydrogen adduct radicals of $5.0 \times 10^{-4} \text{ M}$ benzil (40 and 150 μs) and its derivatives ($1.0 \times 10^{-3} \text{ M}$) in ethanol at 150 μs .

these bands are reported [16] to be $8.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ and $2.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ respectively. In Fig. 3, the absorption of hydrogen adduct radicals of other derivatives of benzil shows two bands similar to those of benzil.

For 2,2'-dichlorobenzil, the bands are blue shifted and for 2,2'-dimethylbenzil the two bands become closer. In the case of mesitil one band appears at 390 nm.

According to the X-ray crystal structure of mesitil [25] the mesityl planes are out of the central —COCO— plane to avoid steric interactions with the *ortho*-methyl groups in the other half of the molecule. The molecular

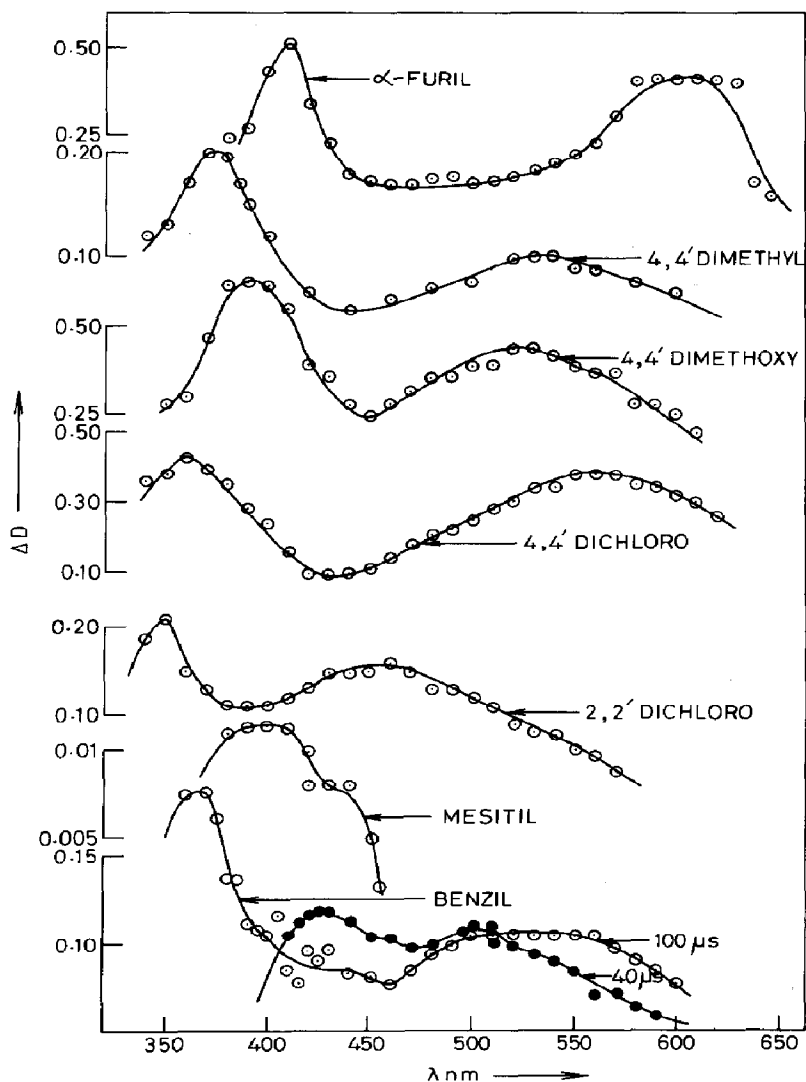


Fig. 4. Absorption spectra of radical anions of 5.0×10^{-4} M benzil with 1.0×10^{-4} M triethylamine (40 and 100 μ s) and its derivatives (1.0×10^{-3} M) with 1.0×10^{-2} M triethylamine in ethanol at 150 μ s.

orbital calculation for benzil [26, 27] shows that the orientation of the phenyl group to the central $-\text{COCO}-$ plane has a significant effect on the transition energies of its hydrogen adduct radical.

The ground state absorption of 2,2'-dichlorobenzil at 380 nm is similar to that of benzil. Thus the shorter wavelength shift of the radical spectra might be due to the conformation being dissimilar to that of the hydrogen adduct radical of benzil.

The hydrogen adduct radicals of benzil and its derivatives dissociate to the respective radical anion in the presence of a base in ethanol. In Fig. 4, the radical anion spectra in ethanol are presented. By keeping the concentra-

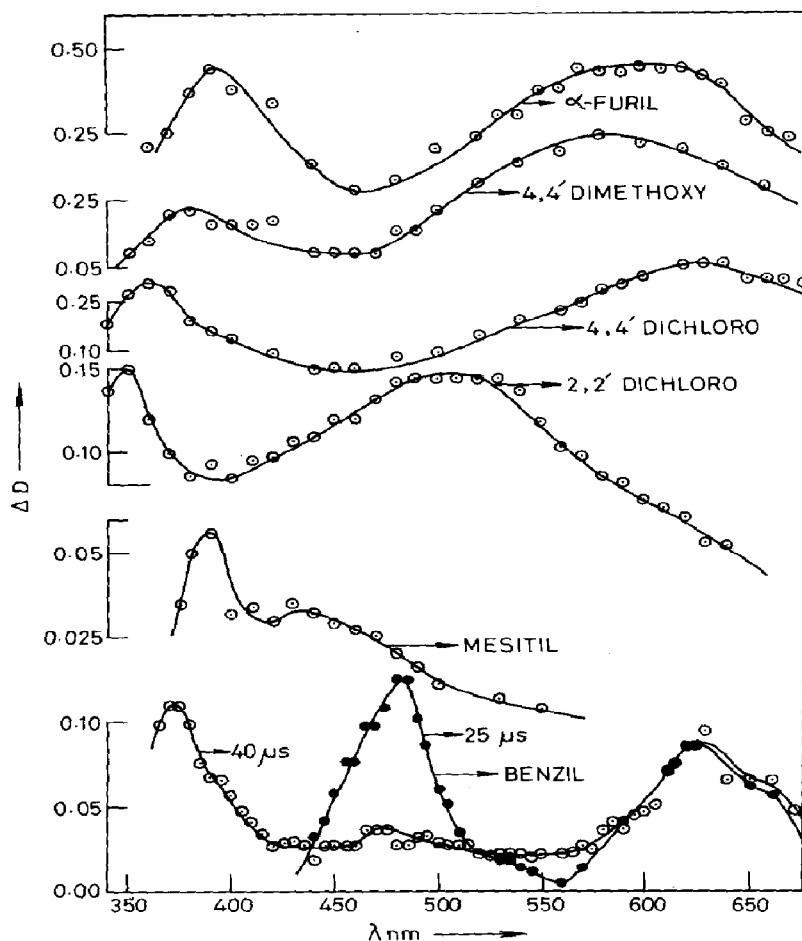


Fig. 5. Absorption spectra of radical anions of 5.0×10^{-4} M benzil with 1.0×10^{-4} M triethylamine (25 and 40 μ s) and its derivatives (1.0×10^{-3} M) with 1.0×10^{-2} M triethylamine in acetonitrile at 150 μ s.

tion of triethylamine low enough (1.0×10^{-4} M) in ethanol, we find a growth of anion at 540 nm and the decay of the hydrogen adduct radical of benzil at 430 nm when benzil (5.0×10^{-4} M) is flash excited. The time-resolved spectra (Fig. 4) and kinetics (see Fig. 6) of radical anion growth and hydrogen adduct radical decay indicate the radical as the precursor of the radical anion. With relatively high base concentration the radical decay goes beyond our instrumental time resolution. The radical anion spectra of the other derivatives of benzil in ethanol solvent are shown in Fig. 4. The absorption of 2,2'-dichlorobenzil and 2,2',4,4',6,6'-hexamethylbenzil anion absorption have been shifted to shorter wavelengths compared with other anion spectra. For mesitil we obtain only one band. Although we were unable to record the triplet-triplet and hydrogen adduct radical spectra of α -furyl, we recorded the radical anion spectra of α -furyl, a maximum appearing at 620 nm.

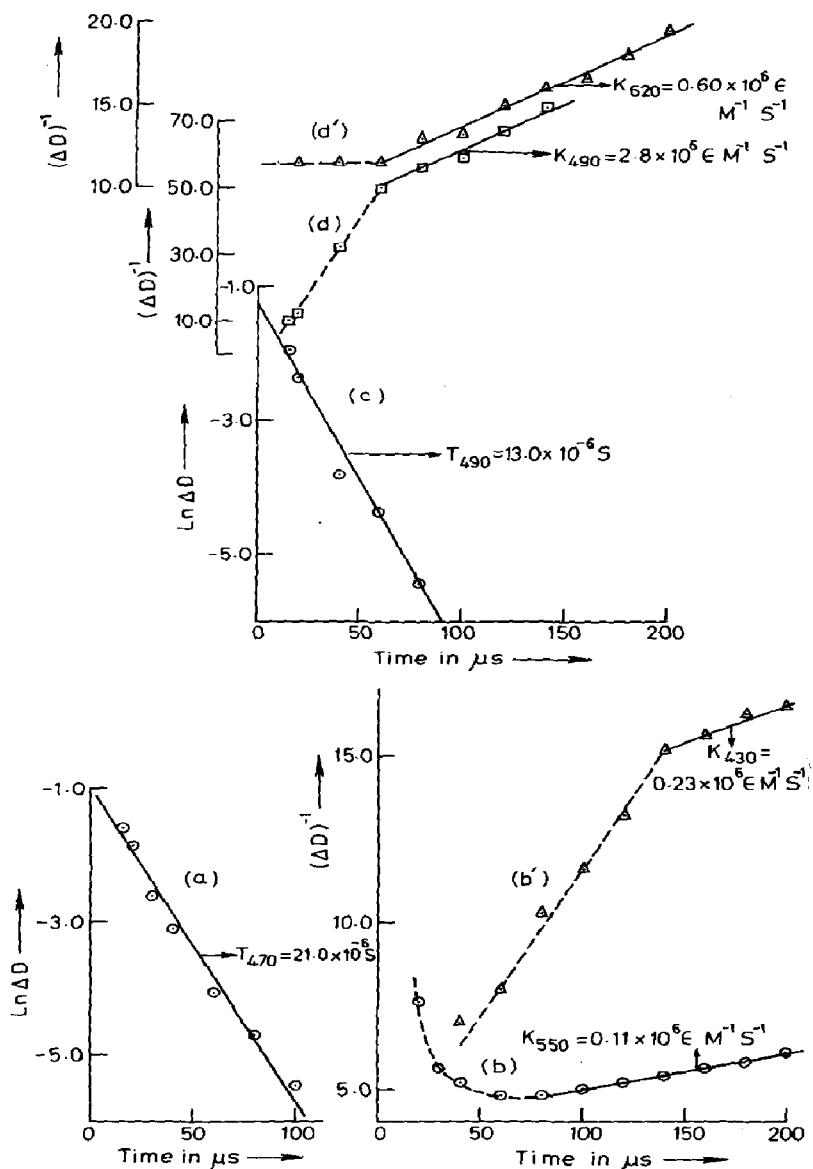


Fig. 6. Decay kinetics of benzil at room temperature. (a) Triplet decay in benzene of benzil (5.0×10^{-4} M). (b) In ethanol, [benzil] = 1.0×10^{-3} M and [triethylamine] = 1.0×10^{-4} M at 550 nm, (b') at 430 nm. (c) In acetonitrile, triplet decay of benzil (5.0×10^{-4} M); with triethylamine (1.0×10^{-4} M): (d') at 620 nm, (d) at 490 nm.

The spectra of radical anions in a polar medium such as acetonitrile are different from those in ethanol (Fig. 5). The absorption band of the benzil anion is shifted to 620 nm in acetonitrile from 540 nm in ethanol. Using a low concentration of triethylamine in acetonitrile both the benzil triplet and the radical anion are found simultaneously at shorter times

(25 μ s). By a careful kinetic analysis of the absorption at 490 and 620 nm (Fig. 6), we could show that the decay of the 490 nm absorption follows two different kinetic pathways, the first due to the triplet is fast, and the second due to the radical anion is slow, whereas the 620 nm absorption initially remains constant without growing tendency. This suggests that the anion in acetonitrile is formed directly from the triplets and not via hydrogen adduct radical dissociation as found in ethanol solvent.

The shift of the benzil radical anion absorption from 540 nm in ethanol to 620 nm in acetonitrile has been studied carefully in a benzene-acetonitrile mixture. On varying the solvent polarity for the different mixtures, the absorption band does not shift continuously; instead there is an abrupt shift. In the solvent mixture where the concentration of benzene is more than 20% the band appears at 560 nm. For comparison, we studied α -furyl anion absorption in the same solvent mixture. In the case of α -furyl, the band at 620 nm does not change even with a large excess of benzene. As with the mesityl anion, the α -furyl anion absorption remains unchanged on changing the solvent from ethanol to acetonitrile. Thus the large shift of the benzil anion absorption could not be due to the change in polarity of the solvent and it could not be due to hydrogen bonding in ethanol. The α -furyl [28] and mesityl [29] are rigid and do not undergo change in conformation, puckered in the case of α -furyl and with a planar —COCO— group with twisting mesityl groups in the case of mesityl. The puckered triplet of benzil phosphoresces in the same wavelength region as does α -furyl. Thus the 620 nm absorption of the benzil radical anion in acetonitrile could be attributed to its puckered conformation.

The decay of hydrogen adduct radicals and radical anions follows second-order kinetics. The decay of radical anions is at least ten times slower than that of the radicals (Table 1). The first-order decay kinetics of the dichlorobenzil radical anions in ethanol (Table 1) are unusual because the decay of all other benzil anions follows second-order kinetics. The lifetimes of the 2,2'- and 4,4'-dichloro derivatives are quite long (0.33 s and 0.41 s respectively). The first-order kinetics might be due to the presence of chloro groups which form an ion pair complex with the counter positive ion and the charge neutralization which takes place following a slow first-order process. The reduction potentials of benzil and its derivatives are given in Table 1. It is noted that α -furyl has the maximum tendency to be reduced in the series. Of the methyl, methoxy and chloro derivatives of benzil, the chloro derivatives have the greatest tendency to be reduced.

Acknowledgments

Thanks are due to the Council of Scientific and Industrial Research, India, for awarding a fellowship to Jaya Bhattacharya and to the University Grants Commission, India, for awarding fellowships to Jibandhan Bando-padhyay and Gour Krishna Das Mohapatra under the Departmental Special

Assistance programme in chemistry under the University Grants Commission, India.

References

- 1 C. J. Brown and R. Sadanaga, *Acta Crystallogr.*, **18** (1965) 158.
- 2 S. C. Bera, R. K. Mukherjee and M. Chowdhury, *Indian J. Pure Appl. Phys.*, **7** (1969) 345.
- 3 T. S. Fang, R. E. Brown and L. A. Singer, *J. Chem. Soc., Chem. Commun.*, (1978) 116.
- 4 S. C. Bera, R. K. Mukherjee and M. Chowdhury, *J. Chem. Phys.*, **51** (1969) 754.
- 5 D. J. Morantz and A. J. C. Wright, *J. Chem. Phys.*, **53** (1970) 1622.
- 6 J. F. Arnett and S. P. McGlynn, *J. Phys. Chem.*, **79** (1975) 626.
- 7 T. S. Fang, R. E. Brown, C. L. Kwan and L. A. Singer, *J. Phys. Chem.*, **82** (1978) 2489.
- 8 K. Bhattacharya, D. S. Roy and M. Chowdhury, *J. Lumin.*, **22** (1980) 95.
- 9 I. Y. Chan and B. A. Heath, *J. Chem. Phys.*, **71** (1979) 1070.
Y. Teki, T. Takui, M. Hirai and K. Itoh, *Chem. Phys. Lett.*, **89** (1982) 163.
- 10 S. Yamauchi and N. Hirota, *J. Phys. Chem.*, **88** (1984) 4631.
A. I. Grant and K. A. McLauchan, *Chem. Phys. Lett.*, **101** (1983) 120.
- 11 R. W. Fessenden, P. M. Carton, H. Shimamori and J. C. Scaiano, *J. Phys. Chem.*, **86** (1982) 3809.
- 12 G. Porter and M. W. Windsor, *Proc. R. Soc. London, Ser. A*, **245** (1958) 238.
- 13 A. Beckett, A. D. Osborne and G. Porter, *Trans. Faraday Soc.*, **60** (1964) 873.
- 14 M. W. Encinas and J. C. Scaiano, *J. Am. Chem. Soc.*, **101** (1979) 7740.
- 15 D. Griller, J. A. Howard, P. R. Marriott and J. C. Scaiano, *J. Am. Chem. Soc.*, **103** (1981) 619.
- 16 E. Hayon, T. Iyata, N. N. Lichtin and M. Simic, *J. Phys. Chem.*, **76** (1972) 2071.
- 17 B. Klein, *J. Am. Chem. Soc.*, **63** (1941) 1474.
- 18 M. Gomberg and F. J. Yannatta, *J. Am. Chem. Soc., Part II*, **51** (1929) 2238.
- 19 H. H. Hodgson and W. Rosenberg, *J. Chem. Soc., Part I*, (1930) 14.
- 20 A. I. Vogel, *Textbook of Practical Organic Chemistry*, English Language Book Society and Longman, 1978, 4th edn., pp. 806 - 807.
- 21 R. C. Fuson and J. Corse, *J. Am. Chem. Soc.*, **60** (1938) 2026.
- 22 R. C. Fuson and A. I. Rachlin, *J. Am. Chem. Soc.*, **68** (1946) 343.
- 23 A. I. Vogel, *Textbook of Practical Organic Chemistry*, English Language Book Society and Longman, 1978, 4th edn., pp. 266 - 267, 268, 277.
- 24 D. S. Roy, K. Bhattacharya, S. C. Bera and M. Chowdhury, *Chem. Phys. Lett.*, **69** (1980) 134.
- 25 S. C. Biswas and R. K. Sen, *Chem. Phys. Lett.*, **94** (1983) 415.
- 26 J. P. Lowe, *Quantum Chemistry*, Academic Press, New York, 1978, p. 246.
- 27 G. K. Das Mohapatra, J. Bhattacharya, J. Bandopadhyay and S. Chandra Bera, Simple molecular orbital calculations of benzils, unpublished work.
- 28 R. Debnath, S. K. Chatterjee and S. C. Bera, *Indian J. Chem., Ser. A*, **24** (1985) 334.
- 29 S. C. Bera, B. Karmakar and M. Chowdhury, *Chem. Phys. Lett.*, **27** (1974) 397.