

PHOTOREACTIONS OF BIACETYL WITH TETRAMETHYL-1,3-DIOXOLE AND 1,1-DIETHOXYETHENE: SOLVENT DEPENDENCE OF THE PRODUCT QUANTUM YIELD AS AN INDICATION OF THE COMPETITION BETWEEN PRODUCT FORMATION AND IONIC PHOTODISSOCIATION

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Summary

The product quantum yields of the photoreactions between singlet excited biacetyl (1) and tetramethyl-1,3-dioxole (2) and between triplet excited 1 and 1,1-diethoxyethene (3) decrease as the dielectric constant ϵ of the solvent increases. This solvent effect is explained in terms of the competition between product formation and ionic photodissociation. The dependence of the calculated free enthalpies of the solvated ion pairs ($1_s^- \cdots 2_s^+$) and the dissociated ion radicals ($1_s^- + 2_s^+$) on ϵ clearly demonstrates that ionic photodissociation becomes exothermic in solvents with $\epsilon \geq 5$.

1. Introduction

The dependence of quantum yields for ionic photodissociation on solvent polarity has been demonstrated by Taniguchi *et al.* [1] for the pyrene-*N,N*-dimethylaniline system by means of laser photolysis, transient photoconductivity and transient absorption measurements. They showed that the yield of ionic photodissociation increased when the dielectric constant of the solvent was increased, whereas the calculated free energies of the solvated ion pair and the dissociated ion radicals decreased. The same relation was found for the triplet benzophenone-*N,N*-diethylaniline-*N,N*-dimethyl-*p*-toluidine system by Arimitsu *et al.* [2]. The solvent-dependent competition between ionic photodissociation and hydrogen abstraction was demonstrated by measuring the absorbance of both the benzophenone anion and the ketyl radical. The sum of the quantum yields of ionic photodissociation and photoreduction for this system was estimated to be unity. Lewis [3] reported that the quantum yield of cycloadduct formation for the 2,5-diethyl-1,4-hexadiene-diphenylvinylene carbonate system decreased with increasing dielectric constant.

Masuhara *et al.* [4] proposed the empirical equations

$$\ln\left(\frac{1}{\Phi_{\text{diss}}} - 1\right) = \frac{p}{\epsilon} + q \quad (1)$$

$$\ln\left(\frac{1}{\Phi_{\text{diss}}}\right) = \frac{p'}{\epsilon} + q' \quad (2)$$

for the solvent dependence of the ionic photodissociation quantum yield Φ_{diss} for some 1,2,4,5-tetracyanobenzene electron donor-acceptor complexes and the pyrene-*N,N*-diethylaniline exciplex system. ϵ is the dielectric constant and p and q are constants independent of ϵ . These relations were explained using Onsager's ion recombination model (eqn. (2)) and the Horiuchi-Polanyi relation for the activation energy (eqn. (1)). In the present study this model is applied to the photoreactions of biacetyl (1) with tetramethyl-1,3-dioxole (2) [5] and 1,1-diethoxyethene (3) [6] by measuring the product quantum yields in various solvents (Fig. 1).

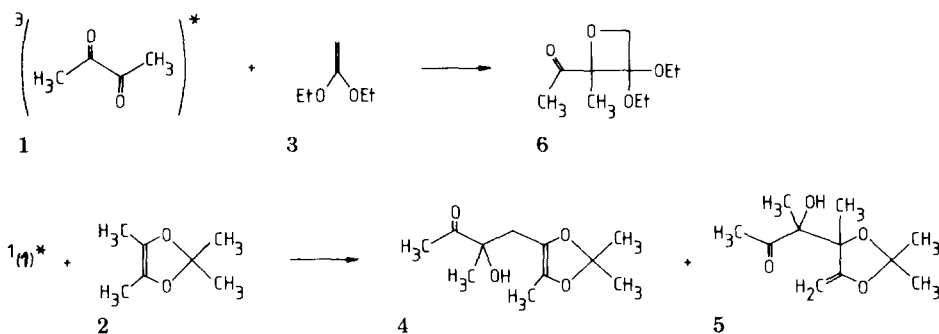


Fig. 1. Isolated products of the reactions of triplet biacetyl (1) with 1,1-diethoxyethene (3) and of singlet biacetyl (1) with tetramethyldioxole (2).

2. Experimental details

The complete details of the preparation, isolation and identification of the photoproducts 4-6 together with other results will be published elsewhere [5, 6].

Compounds 1, 2 [7] and 3 [8] were distilled under nitrogen. 1 was distilled at room temperature under reduced pressure directly before use, particularly when it was employed for kinetic measurements.

The solvents (Merck Uvasol) were purged with argon before use. The quantum yields of product formation were measured using solutions containing 0.2 M 1 and either 0.2 M 2 or 0.02 M 3 which had been irradiated up to a maximum of 5% conversion.

The Stern-Volmer data for the luminescence quenching of 1 by 2 and 3 in benzene ($K_{\text{SV}}(2) = 97.1 \text{ l mol}^{-1}$ and $K_{\text{SV}}(3) = 3.36 \text{ l mol}^{-1}$ for

fluorescence quenching; $K_{SV}(2) = 5.07 \times 10^5 \text{ l mol}^{-1}$ and $K_{SV}(3) = 3.96 \times 10^3 \text{ l mol}^{-1}$ for phosphorescence quenching) indicate that the photoreaction with **2** mainly occurs via S_1 (96% fluorescence quenching with **1**) and that with **3** occurs via T_1 (about 5% or less fluorescence quenching but 100% phosphorescence quenching of **1**) at the chosen concentrations. The results of further investigations in which the concentrations were varied and **1** was sensitized using benzophenone showed that the S_1 and T_1 reactivities of **1** were identical [6].

The solutions were irradiated using an Osram HBO 500 W lamp and a filter solution of copper sulphate, sodium nitrite and concentrated ammonium hydroxide with a window between 400 and 460 nm. The quantum yields were determined using a potassium ferrioxalate actinometer. Quantitative determinations of product formation were performed using vapour phase chromatography on a silicone OV 17 column using a Fractovap 2101 gas chromatograph (Carlo Erba) and an SP 4000 integrator (Spectra Physics). The internal standard was dibutyl oxalate.

The oxidation potentials of **2** and **3** and the reduction potential of **1** were measured using cyclic voltammetry with a platinum working electrode in acetonitrile and a saturated calomel reference electrode at a scan rate of 100 mV s^{-1} :

$$E_{1/2}(1^-|1) = -1.23 \text{ V (1 mM; 100 mM } n\text{-Bu}_4\text{NBF}_4)$$

$$E_{1/2}(2|2^+) = 0.72 \text{ V (1 mM; 100 mM LiClO}_4)$$

$$E_{1/2}(3|3^+) = 1.15 \text{ V (1 mM; 100 mM LiClO}_4)$$

The cyclic voltammograms of **1** and **3** both exhibit totally irreversible electrochemical processes, whereas the oxidation of **2** at 0.72 V is reversible. In the latter case two other electrochemical processes occur, a reversible process at 0.2 V and an irreversible process at 1.6 V.

3. Results and discussion

The free enthalpies $\Delta G(1_s^- \cdots 2_s^+)$ and $\Delta G(1_s^- + 2_s^+)$ of the solvated ion pair and the dissociated ion radicals respectively for the 1-2 system above the ground state in various solvents are calculated as follows [1]:

$$\Delta G(1_s^- \cdots 2_s^+) = \Delta G(1_s^- + 2_s^+) - \frac{e^2 N_A}{4\pi\epsilon_0\epsilon D} \quad (3)$$

$$\Delta G(1_s^- + 2_s^+) = F\{E_{1/2}(2|2^+) - E_{1/2}(1^-|1)\} + \frac{e^2 N_A}{4\pi\epsilon_0 R} \left(\frac{1}{\epsilon} - \frac{1}{37.5} \right) \quad (4)$$

where $F = 96490 \text{ C}$, $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$, $\epsilon_0 = 8.854 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$, R is the ionic radius which is assumed to be 0.35 nm [1] and D is the distance between the 2^+ and the 1^- ions which is assumed to be 0.70 nm [1].

The results are shown in Table 1 and Fig. 2 together with the product quantum yield and clearly demonstrate that the electron transfer becomes exothermic in solvents with $\epsilon \geq 5$. As a consequence the Φ_p - ϵ and ΔG - ϵ curves have similar shapes.

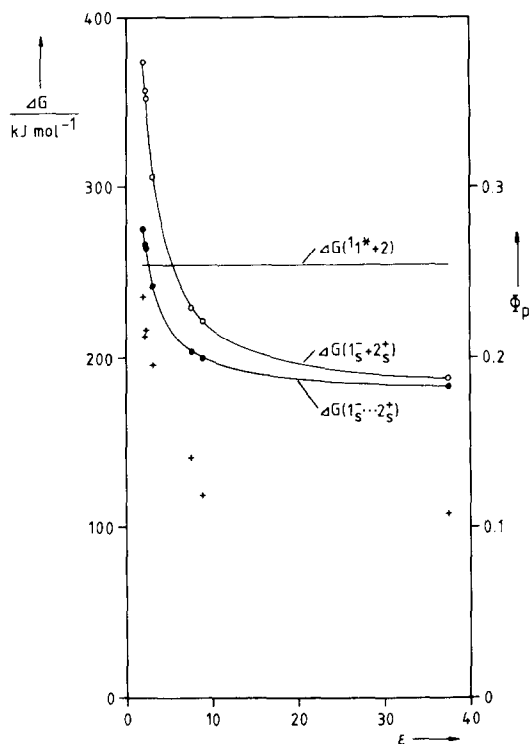


Fig. 2. Plots of ΔG and $\Phi_p(4 + 5)$ (+) vs. ϵ (see Table 1). $\Delta G(1^* + 2) = 255$ kJ mol⁻¹ is equivalent to the fluorescence maximum at 470 nm.

TABLE 1

Free enthalpies $\Delta G(1_s^- \cdots 2_s^+)$ and $\Delta G(1_s^- + 2_s^+)$ calculated according to eqns. (3) and (4) and measured product quantum yields of 4 and 5 in various solvents

Solvent	ϵ	$\Delta G(1_s^- \cdots 2_s^+)$ (kJ mol ⁻¹)	$\Delta G(1_s^- + 2_s^+)$ (kJ mol ⁻¹)	$\Phi_p(4 + 5)$
Cyclohexane	2.02	276	374	0.236
1,4-dioxane	2.21	267	357	0.213
Benzene	2.28	265	352	0.217
Di- <i>n</i> -butyl ether	3.08	242	306	0.196
Tetrahydrofuran	7.58	204	230	0.141
Dichloromethane	8.93	200	222	0.119
Acetonitrile	37.5	183	188	0.102

Similar results have been reported by Arimitsu *et al.* [2] for the tetracyanobenzene-toluene and pyrene-*N,N*-diethylaniline systems where electron transfer becomes exothermic in solvents with $2 < \epsilon < 10$.

If it is assumed that there are only two reaction pathways for the dissociative excited state (exciplex), *i.e.* ionic dissociation with the rate constant k_{diss} and product formation with the rate constant k_p , the ionic photodissociation yield Φ_{diss} in eqns. (1) and (2) can be substituted by

$$\Phi_{\text{diss}} = 1 - \Phi_p \quad (5)$$

where

$$\Phi_p = \frac{k_p}{k_p + k_{\text{diss}}} \quad (6)$$

It is assumed that the rate constant k_p for product formation is independent of ϵ [2]. Therefore the modified forms of eqns. (1) and (2) are

$$\ln\left(\frac{\Phi_p}{1 - \Phi_p}\right) = \frac{p}{\epsilon} + q \quad (7)$$

$$\ln\left(\frac{1}{1 - \Phi_p}\right) = \frac{p'}{\epsilon} + q' \quad (8)$$

The results for the 1-2 and 1-3 systems are given in Table 2 and Fig. 3. The parameters of the linear regression equations are given in Table 3.

The generation of solvated ion radicals in solvents with $\epsilon \leq 5$ is endothermic for the singlet 1-2 system (Fig. 2). Therefore it is reasonable to assume that no ionic photodissociation takes place in cyclohexane ($\Phi_{\text{diss}}^{\text{cy}} = 0$). Since the highest product quantum yields in cyclohexane are less than

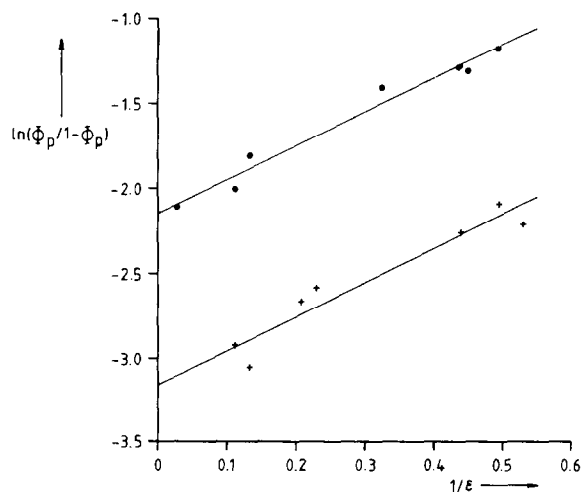


Fig. 3. Plots of $\ln\{\Phi_p/(1 - \Phi_p)\}$ vs. $1/\epsilon$ according to eqn. (7): ●, $1^* + 2$ system; +, $3^* + 3$ system.

TABLE 2
Dependence of the quantum yields on solvent polarity

Solvent	$1/\epsilon$	$\Phi_p(6)$	$\ln\{\Phi_p/(1-\Phi_p)\}^a$		$\ln\{1/(1-\Phi_p)\}^b$		$\ln(1/\Phi_{diss})^c$
			4 + 5 d	6	4 + 5 d	6	
n-hexane	0.532	0.099	-1.175	-2.208	0.269	0.104	2.519
Cyclohexane	0.495	0.110	-1.307	-2.091	0.240	0.117	2.328
1,4-dioxane	0.452	0.095	-1.411	-2.254	0.218	0.100	1.775
Benzene	0.325	0.070	-1.807	-2.587	0.152	0.073	0.910
Di-n-butyl ether	0.230	0.065	-2.002	-3.055	0.127	0.046	0.702
Diethyl ether	0.208	0.051	-2.111	-2.924	0.114	0.052	0.612
Chloroform	0.132						
Tetrahydrofuran	0.112						
Dichloromethane	0.027						
Acetonitrile							

^a According to eqn. (7).

^b According to eqn. (8).

^c According to eqn. (12).

^d For absolute quantum yields see Table 1.

TABLE 3

Values and standard deviations of the parameters in eqn. (7) for the biacetyl-tetramethyl-1,3-dioxole and biacetyl-1,1-diethoxyethene systems

System	q	p	q'	p'
$^1\mathbf{1}^* + \mathbf{2}$	-2.14 ± 0.05	1.97 ± 0.15	0.103 ± 0.006	0.327 ± 0.019
$^3\mathbf{1}^* + \mathbf{3}$	-3.16 ± 0.09	2.01 ± 0.26	0.034 ± 0.006	0.150 ± 0.017

unity, we assume that there is a third reaction pathway comprising a deactivation step with rate constant k_{de} leading to the ground state educt molecules. The competition between ionic photodissociation (the existence of which is proved by the detection of the free-radical ions in electron spin resonance (ESR) spectra) and product formation [5, 6] shows that the effects of solvent polarity on k_{diss} or k_p and k_{de} are completely different. Although Lewis and coworkers [9] reported some solvent polarity effects on exciplex fluorescence quantum yields and lifetimes in the diphenylvinylene carbonate-dimethyl hexadiene system, we did not observe such an unusual dependence on ϵ . Therefore, to a first approximation, we assume like Masuhara *et al.* [4] that k_p and k_{de} are independent of ϵ .

The ionic photodissociation quantum yield Φ_{diss}^ϵ in a solvent with dielectric constant ϵ can now be calculated:

$$\frac{k_{de}^{cy}}{k_p^{cy}} = \frac{\Phi_{de}^{cy}}{\Phi_p^{cy}} = \frac{\Phi_{de}^\epsilon}{\Phi_p^\epsilon} \quad (9)$$

$$\Phi_p^{cy} + \Phi_{de}^{cy} = 1 \quad (10)$$

$$\Phi_p^\epsilon + \Phi_{de}^\epsilon + \Phi_{diss}^\epsilon = 1 \quad (11)$$

(for $\epsilon > 2.02$)

$$\Phi_{diss}^\epsilon = 1 - \Phi_p^\epsilon \left(1 - \frac{\Phi_{de}^{cy}}{\Phi_p^{cy}} \right) \quad (12)$$

The ionic dissociation yields calculated for the singlet 1-2 system are listed in Table 2. The following linear regression equation is then obtained from eqn. (2):

$$\ln \left(\frac{1}{\Phi_{diss}} \right) = 0.335 \pm 0.106 + (4.60 \pm 0.36) \frac{1}{\epsilon}$$

This equation indicates that the result is consistent with our assumptions of competition between the solvent-dependent (k_{diss}) and solvent-independent (k_p and k_{de}) reaction pathways.

It should be noted that the plots in Fig. 3 exhibit equal slopes but different intercepts. This can be explained in terms of the theory developed by Mataga and coworkers using the Horiuchi-Polanyi relation for the activation

energy [4, 10]. According to this model the activation energy for dissociation is a function of the energy of the resulting radical ions which is determined by a solvent-independent term (intercept) and a solvent-dependent term (slope $\times 1/\epsilon$). This finally leads to eqn. (1) for the dependence of the dissociation quantum yield on the solvent polarity and its modified form (eqn. (7)) using our measured product quantum yields. In this case the intercept is determined by substrate-specific parameters such as the rate constants of deactivation and dissociation in a standard solvent with dielectric constant ϵ° and consequently different values are obtained for different educt molecules. Analogous interpretations can be obtained using Onsager's ion recombination model [4, 10]. The fraction α of the dissociative state in the encounter collision leading to the formation of the ion pair, which is followed by recombination and dissociation, corresponds to the intercept of eqn. (2) (or the modified eqn. (8)) and is assumed to be independent of ϵ . Different intercepts again indicate that α depends on substrate-specific parameters. The slopes obtained for both models can be used to compare the interactions between the dipolar intermediates and the solvent. Equal slopes demonstrate that these interactions are similar even for different donor molecules (2 and 3) and different spin configurations ($^11^* + 2$ and $^31^* + 3$), indicating a similar reaction mechanism. The same results were obtained for the photoreaction of 1 with 4,5-dimethyl-1,3-dioxole which proceeds via both the S_1 and T_1 states of 1 [6].

4. Conclusion

The observation by ESR spectroscopy of the radical cations of both 2 and 1 during the irradiation of a solution of 1 and 2 in acetonitrile [5, 6] and the solvent dependence of the product quantum yield indicate competition between product formation and ionic photodissociation, which becomes exothermic in solvents with $\epsilon \geq 5$.

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