

PHOTOREACTIONS OF FLUORENONE WITH ELECTRON-RICH ALKENES: RADICAL ION PAIR FORMATION IN POLAR AND NON-POLAR SOLVENTS^{†‡}

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Summary

Flash photolysis studies showed that triplet fluorenone reacts with electron-rich olefins like tetramethyl-1,3-dioxole and tetraethoxyethene to give radical ions and radical ion pairs. The fraction of contact ion pairs and solvent-separated ion pairs was determined in various solvents. Ion pair formation was detected even in non-polar solvents like benzene and cyclohexane, although the formation of solvent-separated ion pairs is endothermic according to Weller and Mataga. The application of the special salt effect confirms our observations of an equilibrium between contact ion pairs and solvent-separated ion pairs. The same technique was used to show that excited fluorenone reacts with triethylamine to give both solvent-separated ion pairs and contact ion pairs in polar solvents or only contact ion pairs in non-polar solvents.

1. Introduction

The optical absorption spectra of alkali metal 9-fluorenone ketyls have been extensively investigated [1]. The concentration, the solvent, the temperature and the cation dependences of the absorption maxima are caused by equilibria between solvent-separated ion pairs (SSIP), monomeric contact ion pairs (CIP), paramagnetic dimers and diamagnetic dimers [1 - 3] (Fig. 1). Peters *et al.* [4] studied the quenching of the π, π^* excited singlet state of fluorenone with 1,4-diazabicyclo[2.2.2]octane (Dabco) utilizing picosecond absorption spectroscopy. The lifetime of the fluorenone radical anion was 60 ps for 1 M Dabco in 2-propanol. It was further shown that radical inter-

[†]Dedicated to Professor Dr. Dietrich Schulte-Frohlinde on the occasion of his 60th birthday.

[‡]This paper forms part IV of the series 'Selectivity and charge transfer in photoreactions of donor-acceptor systems (parts I - III are cited as ref. 6).

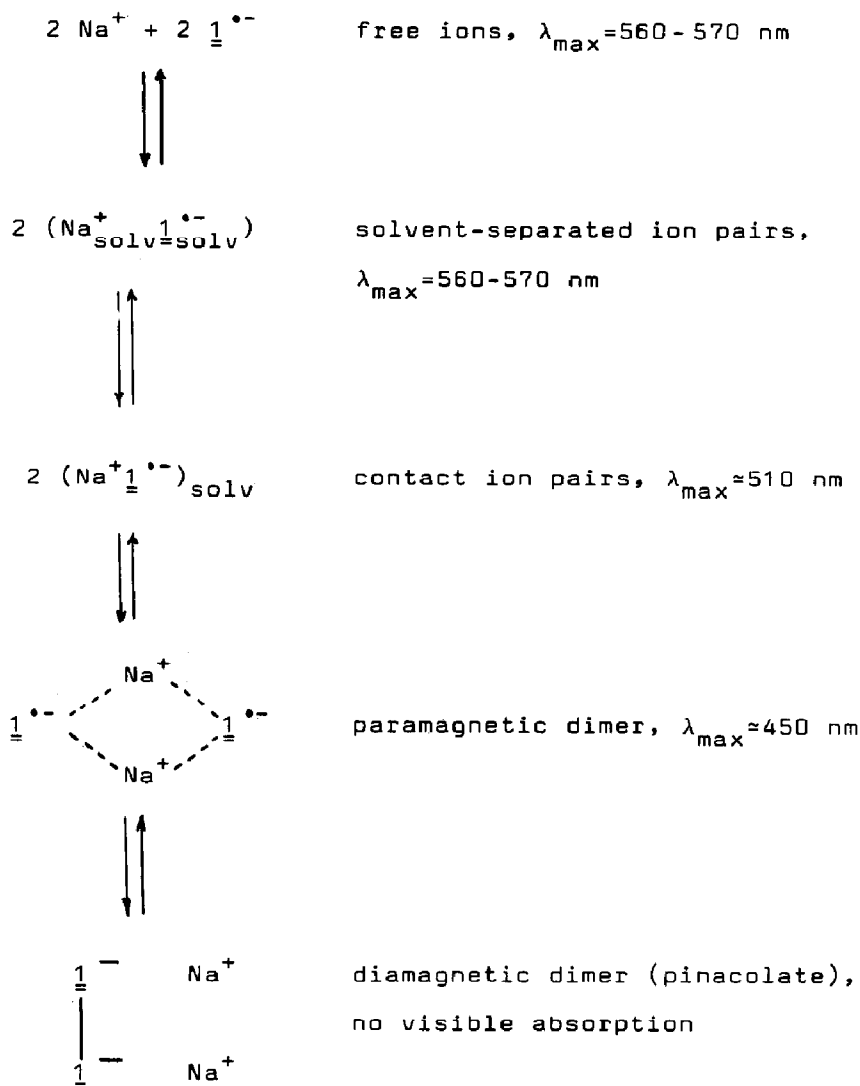
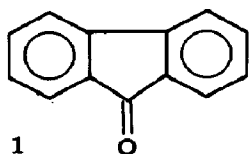


Fig. 1. Equilibria among various forms of sodium 9-fluorenone ketyls [1 - 3].

mediates in the triplet quenching of fluorenone with amines could be detected by means of conventional flash photolysis techniques [5].

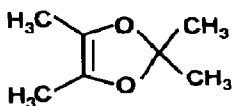
As part of our studies of the photoreactions of ketones with electron-rich olefins [6, 7] we shall show in the present paper that the quenching of triplet fluorenone yields radical ions or radical ion pairs even in non-polar solvents. We studied the transient absorption spectra of the intermediates generated in the photoreaction of triplet fluorenone ($^31^*$) with triethylamine (2), tetramethyl-1,3-dioxole (3) and tetraethoxyethene (4) in various solvents.



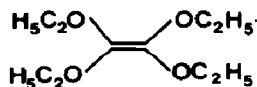
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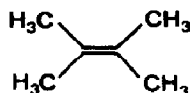
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2. Experimental details

Compound 1 (from EGA-Chemie) was recrystallized several times from petroleum ether and compound 2 was distilled over sodium hydroxide under a nitrogen atmosphere. Compounds 3 [8] and 4 [9] were synthesized according to procedures in the literature, and tetramethylethene (5) was obtained from EGA-Chemie. Benzene, cyclohexane and acetonitrile were purchased from Fluka (spectrophotometric grade) and were used without further purification. Tetrahydrofuran (Fluka; spectrophotometric grade) was distilled over sodium and purified by absorptive filtration over activated aluminium oxide (Woelm). The solutions containing 10^{-3} M 1 and 2×10^{-3} M quencher were purged with argon before use. Singlet quenching is obviously not important at these quencher concentrations [10]. The transient absorption spectra were measured by means of flash photolysis equipment (Applied Photophysics) using a xenon-filled flash lamp with a full width at half-maximum of 16 μs . The photomultiplier signals were recorded using a Tektronix oscilloscope (dual time base 5812 N, dual trace amplifier and dual beam display unit). The half-lives of the transients are in the range 100–200 μs .

Half-peak potentials were obtained by cyclic voltammetry using a platinum electrode *versus* an Ag–AgNO₃ electrode in acetonitrile with $c = 1$ mM. The supporting electrolyte was 0.1 M tetrabutylammonium tetrafluoroborate and the scan speed was 100 mV s⁻¹.

3. Results and discussion

In acetonitrile ³1* and 2 yield SSIP and CIP whereas in benzene solutions only monomeric and dimeric CIP are formed (Fig. 2). When 3 is used as a quencher the absorption spectra (Fig. 3) in benzene and acetonitrile are

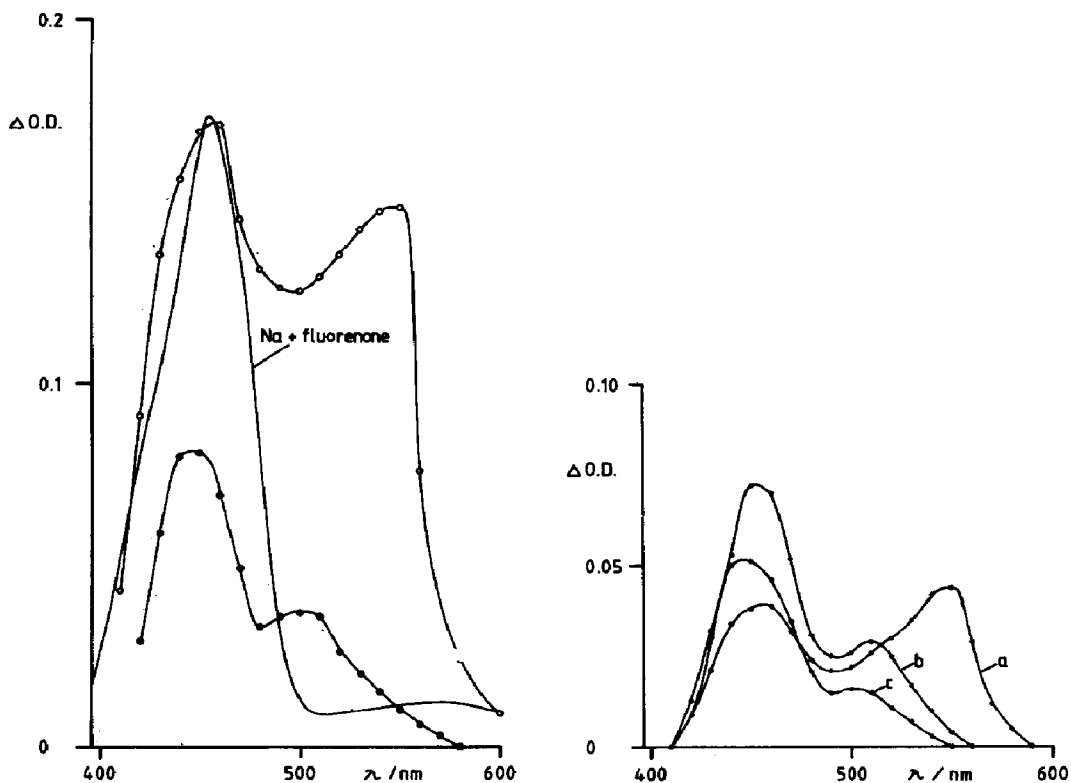


Fig. 2. Transient absorption spectra of 1 and 2 100 μ s after starting the flash: \circ , in acetonitrile; \bullet , in benzene. The relative absorption spectrum of sodium and 0.1 M 1 in acetonitrile is also shown.

Fig. 3. Transient absorption spectra of 1 and 3 100 μ s after starting the flash: curve a, acetonitrile; curve b, benzene; curve c, cyclohexane.

very similar to those obtained for 3. Whereas there is a large fraction of SSIP in acetonitrile, the shoulder at 560 nm indicates only a small fraction of SSIP in tetrahydrofuran (Fig. 4). For benzene and cyclohexane the spectra show only the absorption bands of monomeric and dimeric CIP. The highest fraction of SSIP is obtained with 4 (Fig. 5).

The fractions of each radical ion pair compared with the total amount of the absorbing ion pairs can be calculated omitting spectral overlap and assuming that the extinction coefficients of CIP and SSIP are the same [11]. This is shown for the 1-3 system in Table 1. This calculation neglects the possible formation of the non-absorbing diamagnetic dimeric CIP. Therefore it is not possible to decide whether the smaller amount of paramagnetic radical ion pair formation in non-polar solvents is due to lower ionic photodissociation yields or to the formation of diamagnetic dimers. If only paramagnetic radical ion pairs are considered the ratio [CIP]:[SSIP] is 4.6 for the $^3\text{1}^*-3$ system in tetrahydrofuran, compared with 5 or more for the benzophenone-diethylaniline system in dimethoxyethane [12].

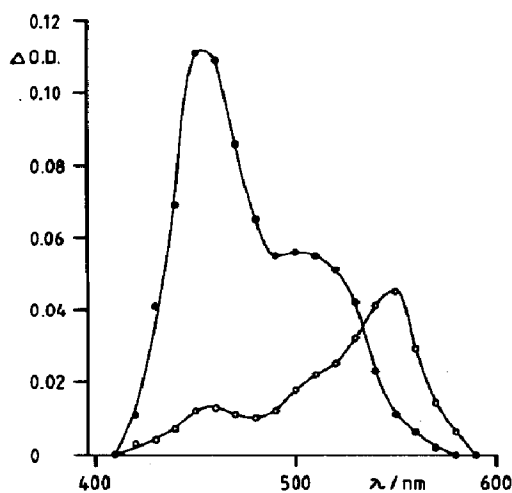
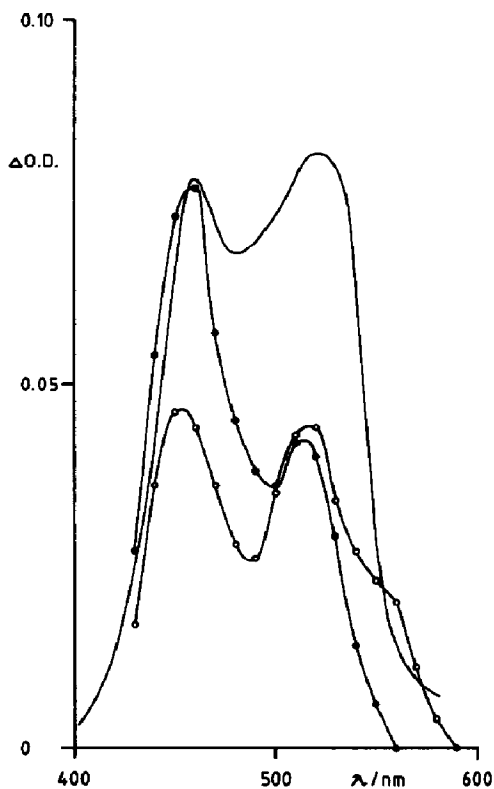


Fig. 4. Transient absorption spectra of 1 and 3 in tetrahydrofuran 150 μ s after starting the flash: \circ , without LiClO_4 ; \bullet , with 0.1 M LiClO_4 . The relative absorption spectrum of sodium and 1 in tetrahydrofuran is also shown.

Fig. 5. Transient absorption spectra of 1 and 4 in acetonitrile 100 μ s after starting the flash: \circ , without LiClO_4 ; \bullet , with 0.1 M LiClO_4 .

TABLE 1

Fraction $F_i = A_i/\sum_i A_i$ in the 1-3 system

Solvent	$F_{\text{CIP-DIMER}}$	$F_{\text{CIP-MONOMER}}$	F_{SSIP}
Cyclohexane	0.76	0.24	0
Benzene	0.71	0.29	0
Tetrahydrofuran	0.42	0.40	0.18
Acetonitrile	0.36	0.24	0.40

The A_i are the absorption maxima of the three different absorbing species.

The addition of LiClO_4 inhibits the formation of SSIP (application of the special salt effect [12]) and increases the fraction of dimeric CIP (Figs. 4 and 5). This corresponds to the smaller equilibrium constant for the equilibrium dimer \rightleftharpoons two monomers in the case of Li^+ compared with larger metal ions [1] or, in our case, to alkene radical ions.

TABLE 2

Oxidation potentials $E_{1/2}(D-D^+)$ of donors and the free enthalpy of SSIP formation in acetonitrile calculated according to Rehm and Weller [13]

Donor (D)	$E_{1/2}(D-D^+)$ (V)	$\Delta G(D^{*+}1^{-})$ (kcal mol ⁻¹)
2	+0.38	-8.0
3	+0.42	-7.1
4	+0.32	-9.4
5	+1.21	+11.1

The excited reduction potential of 1 is $E_{1/2}(^31^*-1^-) = -15.5$ kcal mol⁻¹.

In contrast with the foregoing results we did not obtain any transient absorption with 5 in acetonitrile. This is not surprising because the SSIP formation is endothermic in acetonitrile (Table 2).

9-Hydroxyfluorenyl radicals have not been detected in our systems (i) because of their broad absorption band and their low extinction coefficient compared with the fluorenone radical anion [14], and (ii) because the same absorption bands are obtained for the ³1*-4 system where hydrogen abstraction should not be possible. These results correspond to earlier studies of the dissociation of ketyl radicals which showed that the benzophenone ketyl radical is much more stable than those of fluorenone and benzil [14]. This obvious lack of reactivity towards hydrogen abstraction [15] was also confirmed in our recent investigation of the benzil-4,5-dimethyl-1,3-dioxole system by means of laser flash spectroscopy [7]. There we showed that ketyl radicals are not formed, whereas their quantum yields are in the range 0.8 - 0.9 for the benzophenone-4,5-dimethyl-1,3-dioxole system in various solvents.

To observe radical ion pairs in 1-alkene systems by means of simple microsecond flash measurements is certainly only possible because of the unusual stability of the fluorenone radical anion [14]. Owing to this stability it is also possible to detect the formation of ion pairs even in non-polar solvents like benzene and cyclohexane. According to Rehm and Weller [13] and Taniguchi *et al.* [16] the SSIP formation is endothermic in cyclohexane, e.g. $\Delta G(1^{-}3^{*+}) = +15.1$ kcal mol⁻¹.

Although it is not possible to calculate the free enthalpy of CIP formation because the dipole moments are not known, our results indicate that it should be exothermic in the case of 1-3 and 1-4 systems. Further studies aimed at elucidating the role of CIP and SSIP in product formation are in progress.

Acknowledgments

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