Exciplex Formation and Chemically Induced Electron Polarization

By P. W. Atkins, K. A. McLauchlan,* and P. W. Percival
(*Physical Chemistry Laboratory, South Parks Road, Oxford* OX1 3QZ)

Summary The formation of exciplexes in solution may prolong the lifetime of radical pairs and enhance electron polarization.

Chemically induced electron polarization (CIDEP) gives information about the initial stages of radical formation and the extent of polarization depends both on the rate of separation of the initial radical pair and on the strength of the interaction causing the intersystem mixing. The polarization may be enhanced by constraining the pairs to remain together for longer periods, and since exciplex formation may constitute such a constraint it is possible that CIDEP adds another method to the few capable of being applied to the study of exciplexes. A secondary aspect of exciplex formation may be that the radical pair remains in a configuration that permits S–T_{-1} mixing to occur more extensively than is thought to occur in more labile systems: this modifies the type of polarized spectrum that can be produced.

The e.s.r. detection of the ketyl $Ph_2\dot{C}OH$ during the photolysis of solutions of benzophenone in the presence of triethylamine has been reported;[1] the photochemical reduction of aromatic ketones by tertiary amines is thought to proceed by an exciplex mechanism:[2] the initial step is electron transfer from the amine to the triplet ketone, followed by proton transfer and electron redistribution.

We have studied such systems by time-resolved e.s.r. spectroscopy,[3] and have compared the results with systems of similar viscosity but in which exciplex formation is not expected.

Studies of $[^2H_{10}]$ benzophenone in Nujol at various temperatures[4] indicate that negligible polarization is to be expected for labile solvents (viscosity *ca.* 1cP at room temperature). However the presence of triethylamine has a dramatic effect, see Table. The results suggest a correlation between the observation of electron polarization and the expectation of exciplex formation. Using the 2 MHz superheterodyne detection mode of our equipment[3] enhancement ratios of the order of -40 were observed. (Even this figure might be limited by the response of the apparatus: there is an apparent diminution of the ratio by a factor of 20 on changing from the fast response mode to the conventional 100 kHz modulation system, and this emphasises the need to use response times that are as short as possible.) As in earlier reports[5,6] the spectra show little hyperfine variation of the polarization and are in net emission; this is in contrast to a number of reports[7–9] of polarized spectra where there is a strong hyperfine dependence, and the integrated spectrum amplitude is absorptive. In no case do we observe the counter-radical of the exciplex pair. In some cases (see Table) the radical anion $D\dot{Q}^-$ is observed: this might be formed by ionization of $D\dot{Q}H$ in the alkaline solution, or it might escape directly from the exciplex radical pair before proton transfer has occurred—we have no evidence for either view and consider that this question does not affect the polarization mechanism.

Table

Precursor	Reagent/solvent	Radical observed	Initial appearance of spectrum
Benzophenone	Nujol	$Ph_2\dot{C}\dot{O}H$	emission
	Et_3N	$Ph_2\dot{C}OH$	emission
	Et_3N/benzene		
	Et_3N/toluene		
	Et_3N/propan-2-ol		
	KOH/propan-2-ol	$Ph_2\dot{C}O^-$	not polarized
	Ph_3N/benzene	none	—
Duroquinone (DQ)			
	Et_3N/propan-2-ol	$\overset{:-}{DQ}$	emission
	Et_3N/t-butyl alcohol		
	Et_3N/propan-2-ol–benzene		
	KOH/propan-2-ol	$D\dot{Q}^-$	not polarized

We suggest that the formation of an exciplex prolongs the radical pair life-time (by ionic association) so that efficient polarization may occur. It is unlikely that this results from the *g*-value mechanism for S–T_0 mixing for two reasons. First, such mixing occurs when the exchange energy approaches zero; by which time it is likely that proton transfer has occurred and the extent of this polarization would then be independent of the earlier existence of the exciplex. Second, in the normal situation that the S level of the radical pair lies below T_0 emission is expected in the spectrum of the radical having the larger *g*-value.[10] The Table shows that the same radicals are observed in emission regardless of their counter-radical: in hydrocarbon solvents $Ph_2\dot{C}OH$ is predicted to be in emission but in the presence of triethylamine enhanced absorption would be expected. The observations could be rationalised as an interchange of the S and T_0 levels in the two cases, but an alternative mechanism involving S–T_{-1} mixing and which is independent of the relative *g*-values of the pair may be more plausible. S–T_{-1} mixing is known to occur in the CIDNP of biradicals,[11,12] where the exchange integral is kept at a large value by the molecular geometry of the 'radical pair', and the formation of an exciplex may bring about a similar situation. The mixing interaction could be a hyperfine mechanism: only a weak m_I^- dependence of the polarization would be expected if the hyperfine interactions in the counter-radical dominate those of the detected radical, this is indeed the case here ($Ph_2\dot{C}O^-$: spread *ca.* 24G; $Et_3\dot{N}^+$: spread *ca.* 175G). Thus polarization occurs during the exciplex configuration step while the ionic radicals are close together; when proton transfer occurs the exciplex dissociates and the radicals move apart (and more S–T_0 mixing might then occur).

Independently of the precise polarization mechanism, the qualitiative result that the formation of an exciplex affects the polarization can be used as a diagnostic test for the presence of an exciplex. We have studied the room-temperature photolysis of t-butyl alcohol solutions of phenoxyacetic acid in the presence of a sensitizer. This reaction has been postulated to occur by an exciplex mechanism.[13] Using duroquinone we obtained a strong, but unpolarised spectrum of the semiquinone radical DQH: this indicates that an exciplex is not involved, for the radical is seen, but it is not polarised.

The exciplex mechanism might also account for the polarization observed by Glarum and Marshall[14] in electrons formed by the photolysis of solutions of alkali metals: the exciplex would then be $M^{+}e^{-}$. Furthermore, singlet-triplet mixing in exciplexes is also thought to be responsible for magnetic field effects on the photostationary state of some photosensitized isomerizations.[15]

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