Mechanism of Charge-transfer Polymerisation: Solvent Regulation of the Photosensitised Reaction of *N*-Vinylcarbazole in the Presence of an Organic Electron-acceptor

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Summary The photosensitised reaction of *N*-vinylcarbazole in the presence of an organic electron-acceptor is systematically explained mainly on the basis of the solvent effect.

ALTHOUGH the photosensitised reaction of *N*-vinylcarbazole (VCZ) in the presence of an electron-acceptor has been the subject of considerable interest, the results reported are rather confusing. We have recently found that the reaction is greatly influenced by impurities in the reagents,[1] the atmosphere,[2] or the solvent.

Typically, cationic polymerisation of VCZ proceeds in the system VCZ-2,4,7-trinitrofluorenone in nitrobenzene *via* VCZ cation-radical ($VCZ^{+\cdot}$).[3] We have reported that cationic polymerisation takes place in the system VCZ-*p*-quinones in benzene.[4] In the system VCZ-*p*-chloranil in methanol or in acetone, on the other hand, cyclodimerisation of VCZ occurs, *via* $VCZ^{+\cdot}$.[5]

We have studied the effect of solvents, especially basic solvents, on the photosensitised reaction of VCZ in the presence of various organic electron-acceptors. In such polar, basic, solvents as acetone, methanol, or acetonitrile (so long as the anion-radical of the electron-acceptor is stable) cyclodimerisation of VCZ generally takes place exclusively, while in less basic solvents such as benzene or nitrobenzene only cationic polymerisation of VCZ occurs.[3,4] The results are listed in the Table. The mechanism of forma-

Formation of the cyclodimer of N-*vinylcarbazole* (VCZ), trans-1,2-*dicarbazylcyclobutane, in polar, basic solvents*[a,b]

Solvent	Yield of cyclodimer (%) Acetone[c]	Acetonitrile[d]	Methanol[e]
Acceptor			
p-Bromanil[f]	50	67	11
p-Chloranil[f]	56	34	24
2,5-Dichloro-*p*-benzoquinone[f]	57	58	27
p-Benzoquinone[f]	51	45	6
Pyromellitic dianhydride[g]	43	56[c]	—
Maleic anhydride[h]	76	75[c]	—
Phthalic anhydride	72	75[c]	—
syn-Trinitrobenzene	44	65[c]	—
Dimethyl terephthalate	63	75[c]	—
Fumaronitrile (FN)[i]	59	28	—
Carbon tetrachloride	54[j]	41[j]	—

[a] The system was evacuated at 10^{-6} mmHg and irradiated at 10—15° for 5 h with light of wavelength longer than 320 nm at a distance of about 2 cm from a 500 W high-pressure mercury lamp.

[b] In the absence of the electron-acceptor, only photo-radical polymerisation of VCZ occurs.[2]

[c] $[\mathrm{VCZ}] = 5 \times 10^{-1}\,\mathrm{M}$, $[\mathrm{Acceptor}] = 5 \times 10^{-3}\,\mathrm{M}$.

[d] $[\mathrm{VCZ}] = 2{\cdot}5 \times 10^{-1}\,\mathrm{M}$, $[\mathrm{Acceptor}] = 2{\cdot}5 \times 10^{-3}\,\mathrm{M}$.

[e] $[\mathrm{VCZ}] = 2{\cdot}5 \times 10^{-2}\,\mathrm{M}$, $[\mathrm{Acceptor}] = 1 \times 10^{-3}\,\mathrm{M}$.

[f] In benzene, cationic polymerisation.

[g] In THF, 32% cyclodimer.

[h] In THF, 44% cyclodimer; in benzene, cationic polymerisation.

[i] In acetone ($[\mathrm{VCZ}] = [\mathrm{FN}] = 5 \times 10^{-1}\,\mathrm{M}$), 61% copolymer; in acetonitrile ($[\mathrm{VCZ}] = [\mathrm{FN}] = 2{\cdot}5 \times 10^{-1}\,\mathrm{M}$), 44% copolymer; in THF ($[\mathrm{VCZ}] = [\mathrm{FN}] = 4 \times 10^{-1}\,\mathrm{M}$), 36% copolymer; in benzene ($[\mathrm{VCZ}] = [\mathrm{FN}] = 4 \times 10^{-1}\,\mathrm{M}$), 23% VCZ homopolymer and 30% copolymer.

[j] VCZ homopolymer.

tion of the cyclodimer, *trans*-1,2-dicarbazylcyclobutane, is reasonably explained as a radical reaction of $\mathrm{VCZ}^{+\cdot}$, formed through photochemical electron-transfer from VCZ to the electron acceptor, with the VCZ monomer as suggested by Ledwith *et al.*[5] Cation-solvation by the basic solvent seems to be responsible for the cyclodimerisation reaction. VCZ monomer is known to be strongly basic, and easily undergoes cationic polymerisation.[6] Thus, in less basic solvents such as benzene or nitrobenzene, cationic reactivity in $\mathrm{VCZ}^{+\cdot}$ predominates over radical reactivity, leading to cationic polymerisation of VCZ. By contrast, in basic solvents such as acetone, acetonitrile, or methanol, cationic reactivity in $\mathrm{VCZ}^{+\cdot}$ may be suppressed due to cation-solvation; hence radical reactivity becomes preferential, leading to the cyclodimerisation reaction. A relative measure of the basicity of the solvent has been determined.[7] In the system VCZ–fumaronitrile (1:1 mole ratio) radical copolymerisation occurred exclusively in basic solvents; in benzene simultaneous cationic homo-polymerisation of VCZ and radical copolymerisation took place.

We suggest the following systematic interpretation of the photosensitised reaction of VCZ in the presence of various organic electron-acceptors, assuming the intermediacy of $\mathrm{VCZ}^{+\cdot}$, evidence for which we have obtained in certain systems by means of flash spectroscopy.[8] (a) VCZ cation-radical exhibits both cationic and radical reactivity. (b) The cationic reactivity of $\mathrm{VCZ}^{+\cdot}$ is shown by its cationic polymerisation, while its radical reactivity generally leads to cyclodimerisation. (c) When the electron-acceptor is a monomer capable of undergoing radical polymerisation or copolymerisation, and is present in relatively large amounts instead of in catalytic amounts, radical copolymerisation takes place in addition to the above two reactions. (d) The choice of the dual reactivity (cation or radical) of $\mathrm{VCZ}^{+\cdot}$ is mainly determined by the basicity, that is, cation-solvating ability, of the solvent.

Additionally, the solvent polarity, the stability of the anion-radical of the electron-acceptor, and the radical-trapping ability of the solvent or of the electron-acceptor, must be noted. When a very weak electron-acceptor is used, the solvent must be polar enough for the ionisation of the excited charge-transfer complex. With maleic anhydride or pyromellitic dianhydride, cyclodimerisation took place even in tetrahydrofuran. However, with a very weak electron-acceptor, *e.g.*, dimethyl terephthalate, cyclodimerisation did not proceed in tetrahydrofuran, occurring only in polar, basic solvents. The anion-radical of the electron-acceptor formed as the counter ion of VCZ^{+} must be stable for the cyclodimerisation to occur. The anion-radical of $\mathrm{CCl_4}$ appears to be unstable and this system did not yield the cyclodimer even in polar, basic solvents. When electron-acceptors which also act as radical-scavengers are present in high concentration, the cyclodimerisation does not take place, as was found in the case of *p*-quinoid compounds. The solvent nitrobenzene is relatively weak in its cation-solvating ability, and at the same time acts as a strong radical-scavenger.

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