Electron Spin Resonance of Transient Negative Ions in the Formation of Donor–Acceptor Charge-transfer Complexes of Solvent–Tetracyanoethylene Systems

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The first-order decay of negative ions from solvent–tetracyanoethylene donor–acceptor charge-transfer complexes has been observed by e.s.r. spectroscopy. A mechanism based upon simultaneous hydrogen-bonded proton and electron hole transfer is used to account for the decay.

THE bonding of some donor–acceptor charge-transfer complexes is sufficiently exothermic to produce the thermally excited triplet state during complex formation. Some of these excited states dissociate into the donor$^{\dot{+}}$ and acceptor$^{\dot{-}}$ radical-ions.[1] Stewart, Eisner, and Carper found that with tetracyanoethylene (TCNE) as the acceptor molecule addition of the donor solvents dimethyl sulphoxide (DMSO), *NN*-dimethylacetamide (DMA), or acetone produced an e.s.r. signal ascribed to the TCNE$^{\dot{-}}$ radical-anion. This signal increased rapidly to a maximum value, then decayed, and this decay was analysed as second-order recombination of the D$^{\dot{+}}$ and A$^{\dot{-}}$ radical-ions. The second-order rate constants obtained were 95·4 ± (1·9) and 83·0 ± (0·4) l./mole/sec. at 25° for DMSO and DMA respectively. In pure solvents the e.s.r. signal of the radical-anion had zero-order dependence on the solvent donor, *i.e.* first-order dependence on the anion itself.

Their scheme neglected proton tunnelling and electron-hopping mechanisms in the annihilation of the A$^{\dot{-}}$ ion

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[1] F. E. Stewart, M. Eisner, and W. R. Carper, *J. Chem. Phys.*, 1966, **44**, 2866; F. E. Stewart and M. Eisner, *Mol. Phys.*, 1967, **12**, 173.

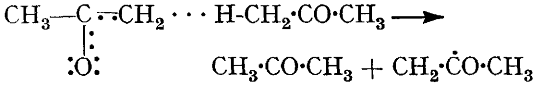
although the latter mechanism was used to account for the spin relaxation of the $\mathrm{D}^{\overset{+}{\cdot}}$ radical-ion and for the absence of the e.s.r. signal of this radical.

In observations on the decay of the e.s.r. signal from some solvent–TCNE complexes we have found a *first-order* decay rate of the TCNE radical-anion, and it is suggested that the rate-determining step in the decay is the activation of an exchange process in the donor–solvent system, possibly as follows:

$$\mathrm{CH_3{\cdot}CO{\cdot}CH_3} + \underset{\text{(A)}}{\mathrm{TCNE}} \longrightarrow [\mathrm{CH_3{\cdot}CO{\cdot}CH_3}]\text{—}\mathrm{A} \quad (1)$$

$$[\mathrm{CH_2{\cdot}CO{\cdot}CH_3}]\text{—}\mathrm{A} \xrightarrow[\text{excitation}]{\text{thermal}} [\mathrm{CH_3{\cdot}CO{\cdot}CH_3}]^{\overset{+}{\cdot}} + \mathrm{A}^{\overset{-}{\cdot}} \quad (2)$$

$$[\mathrm{CH_3{\cdot}CO{\cdot}CH_3}]^{\overset{+}{\cdot}}_{\text{solvent}} \xrightarrow[\text{slow step}]{-\mathrm{H}^+} [\mathrm{CH_3{\cdot}CO{\cdot}\dot{C}H_2}]_{\text{solvent}} \quad (3)$$


(4)

$$\mathrm{CH_3}\text{—}\underset{\underset{:\ddot{\mathrm{O}}:}{|}}{\mathrm{C}}\cdots\mathrm{CH_2}\cdots\mathrm{H\text{-}CH_2{\cdot}CO{\cdot}CH_3} \longrightarrow \mathrm{CH_3{\cdot}CO{\cdot}CH_3} + \mathrm{CH_2{\cdot}\dot{C}O{\cdot}CH_3} \quad (4)$$

The rate-determining step (3) implies that the proton and electron hole transfer is activated across an order of 10^2 molecular dimensions of the solvent terminating at the radical-anion. The electron hole transfer [equation (4)] involves hydrogen-atom transfer in the reverse sense.

The annihilation of $\mathrm{A}^{\overset{-}{\cdot}}$ would come about when the exchanging solvent radical picked up a proton forming the original radical-cation, which could then combine with an $\mathrm{A}^{\overset{-}{\cdot}}$ radical-anion.

$$\mathrm{CH_3{\cdot}CO{\cdot}\dot{C}H_2} + \mathrm{H}^+ \longrightarrow [\mathrm{CH_3{\cdot}CO{\cdot}CH_3}]^{\overset{+}{\cdot}}$$

$$[\mathrm{CH_3{\cdot}CO{\cdot}CH_3}]^{\overset{+}{\cdot}} + \mathrm{A}^{\overset{-}{\cdot}} \longrightarrow [\mathrm{CH_3{\cdot}CO{\cdot}CH_3}]\text{—}\mathrm{A}.$$

or alternatively,

$$\mathrm{CH_3{\cdot}CO{\cdot}\dot{C}H_2} + \mathrm{A}^{\overset{-}{\cdot}} \longrightarrow [\mathrm{CH_3{\cdot}CO{\cdot}CH_2}]\overset{-}{\text{—}}\mathrm{A} \xrightarrow{\mathrm{H}^+} [\mathrm{CH_3{\cdot}CO{\cdot}CH_3}]\text{—}\mathrm{A}.$$

This mechanism would account for the rapid spin relaxation of the positive ion and transfer of the positive site through the viscous solvent

EXPERIMENTAL

The TCNE complexes were prepared by adding solid TCNE to a viscous solvent–polymer mixture in a 35 GHz e.s.r. cavity. The polymers used were atactic polypropylene (supplied by I.C.I., $\bar{M}_{\mathrm{N}} = 1500$, $\bar{M}_{\mathrm{visc}} = 12{,}000$, $\bar{M}_{\mathrm{w}} = 32{,}400$), polystyrene beads (B.D.H.) and polyvinyl acetate beads (B.D.H.)

Solvents were unpurified Laboratory Reagent grade and TCNE was obtained from Ralph N. Emmanuel and was not further purified. The original signals were sufficiently strong, even at the time of observation (*ca.* 3 min. after dissolution), to have already exhausted paramagnetic quenchers such as dissolved oxygen. Flushing the solvent and atmosphere of the e.s.r. cavity with dry oxygen-free nitrogen made no difference to the decay of the radical-anion.

Non-equilibrated dissolution occurred between the solid TCNE and the solvent–polymer matrix, but in all experiments the e.s.r. signal was decaying at the time of measurement.

Despite the incomplete solution of the TCNE and the variability of the consistency of the solvent–polymer matrix, the decay rate of the TCNE anion for any one solvent at room temperature was constant. Each half-life time ($t_{\frac{1}{2}}$) was measured at least six times.

RESULTS AND DISCUSSION

The TCNE radical-anion may be identified by its e.s.r. signal in solution. This consists of nine ^{14}N hyperfine lines of relative intensity 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1 by interaction with the four equivalent nitrogen nuclei, and extreme lines from hyperfine coupling to isotopic ^{13}C.[2]

The ^{14}N hyperfine splitting was 1·56 ± 0·02 gauss and $g = 2{\cdot}0026 \pm 0{\cdot}0002$. The signal we observed had a hyperfine splitting of 1·5 ± 0·1 gauss and $g = 2{\cdot}004 \pm 0{\cdot}002$ and in some cases appeared to have a proton hyperfine splitting of *ca.* 1·5 gauss (Figure 1), although this may have been an artefact of the decay of the signal. The hyperfine components were broadened by magnetic field modulations in excess of 0·1 gauss. The signal was observed at different stages of decay, but on all occasions decayed with a characteristic half-life (Figures 2a, 2b, and 2c).

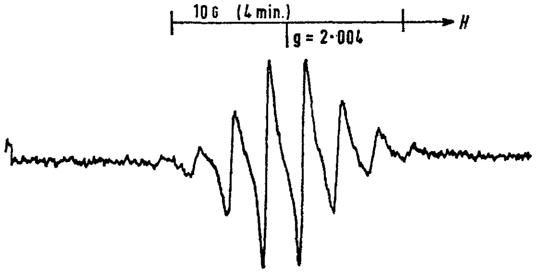


FIGURE 1 E.s.r. signal (35 GHz) of the negative-ion transient product from the donor–acceptor charge-transfer system of acetone–PVA–TCNE

With the variability of the consistency of the solvent–polymer matrix and the degree of TCNE dissolution taken into account, the characteristic half-life was taken as demonstration of a first-order decay mechanism. E.s.r. signals were not observed in the nonprotic solvents carbon tetrachloride, cyclohexane, and isopentane.

We suggest that the rate-determining step is the activation of the solvent-exchange process which results in charge migration. Since all the solvents contain available hydrogen atoms this mechanism implies a common proton-tunnelling effect, similar to the

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[2] W. D. Philips, J. C. Rowell, and S. J. Weissman, *J. Chem. Phys.*, 1960, **33**, 626.

hydrogen-bonding effect in the electrical conduction of water, but also involving transfer of an electron hole. It is unrealistic to ascribe a unique and independent existence to the methanol positive ion in a liquid methanol medium. The methanol positive ion is known from radiation chemical studies[3] to decompose spontaneously into the hydroxymethyl radical which abstracts hydrogen to regenerate methanol and transfer the positive hole. The hydroxymethyl radical produced not by ionization but by hydrogen abstraction from methanol by the hydroxyl radical, regenerates itself in methanol and may be observed by the e.s.r. flow technique.[4] The e.s.r. signals sometimes contained an unresolved spectrum as well as the resolved spectrum. The signals decayed together and we attribute the unresolved signal to the anion, exchange-broadened by concentration effects.

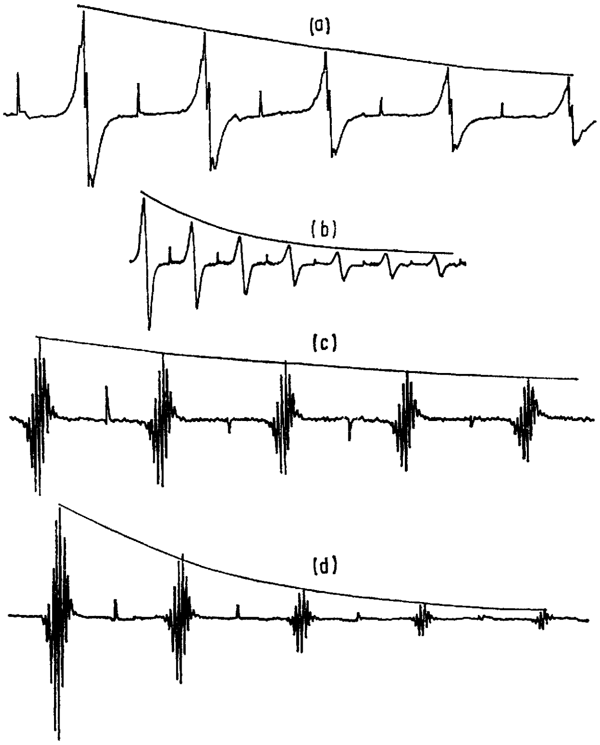

FIGURE 2 Profiles of the decay at 293 K of the 35 GHz e.s.r. signal of the negative ion in the DA systems containing TCNE acceptor and (a) MeOH–PVA (2·5), (b) EtOH–PPA–cyclohexane (1), (c) acetone—PVA (2·5), and (d) DMSO–PVA (2·5). The number in parentheses represents the interval between the consecutive recordings

	$\lambda_{max.}$ (nm.) [a]	ΔH (kcal./mole) [b]	$t_{\frac{1}{2}}$ (min. ± 0·25 min.)	First-order rate constant k_{20° (sec.$^{-1}$) [c]
DMSO–PVA	372	−11·3	2·5	0·28
Methanol–PVA			7·5	0·09
Acetone–PVA	328		7·5	0·09
Vinyl acetate–PVA			11·0	0·06
Ether–PVA	335		20·0	0·03
Benzene–PVA	384	−2·3	∞	0·00
Acetone–PS	328		6·25	0·11
Dioxan–PS	350	−1·83	∞	0·00
Ethanol–PP–CH			2·0	0·34
Methanol–PP–CH			6·5	0·10
Acetone–PP–CH	328		9·0	0·08

PVA = Polyvinyl acetate, PP = atactic polyproplyene, PS = polystyrene, DMSO = dimethyl sulphoxide, CH = cyclohexane.

[a] Denotes centre of charge-transfer absorption band. [b] Enthalpies of complex formation from ref. 1 and R. Vars, L. A. Tripp, and L. W. Pickett, *J. Phys. Chem.*, 1966, **44**, 2866. [c] The first-order rate constant $k = \ln 2/t_{\frac{1}{2}}$.

The decay could be suspended by freezing the systems at temperatures of solid carbon dioxide and boiling liquid nitrogen; it was not significantly altered at 0° C. Our scheme for the decay kinetics and its thermal activation imply an activation energy within kT between $T = 100$ and 200° K. The absolute rate constant measured is largely determined by the pre-exponential factor of the Arrhenius equation, which contains a frequency component and the entropy of activation component. That this pre-exponential factor should determine the absolute rate constant is consistent with our model for the activation of the decay mechanism of the negative ion, since the annihilation of the negative ion is envisaged as an entropy-determined step within a common process for simple proton and electron hole migration.

[9/1663 *Received, September* 30*th*, 1969]

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[3] M. J. Blandemer, L. Shields, and M. C. R. Symons, *J. Chem. Soc.*, 1965, 1127.

[4] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1963, 3119.