

ELECTRON SPIN RESONANCE STUDY OF CHARGE TRANSFER
COMPLEXES OF THE GALVINOXYL RADICAL WITH ELECTRON
ACCEPTORS

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There are several reports of the formation of charge transfer complexes formed by the interaction of molecules with low ionization potentials with those of high electron affinity (1). These complexes can also be formed by photoinduction from donors of relatively high ionization potential such as tetrahydrofuran (THF) (2). Recently Kolodny and Bowers (3) were able to observe, for the first time, both the donor cation radical and the acceptor anion radical simultaneously by esr. Here we wish to report the charge transfer complex formed by the electron transfer from a stable organic radical donor and the use of the simultaneous observation of the donor radical and the acceptor anion radical to determine the thermodynamic parameters controlling the formation of the charge transfer complex. Only unstable radicals have previously been used as donors without simultaneous observation (4).

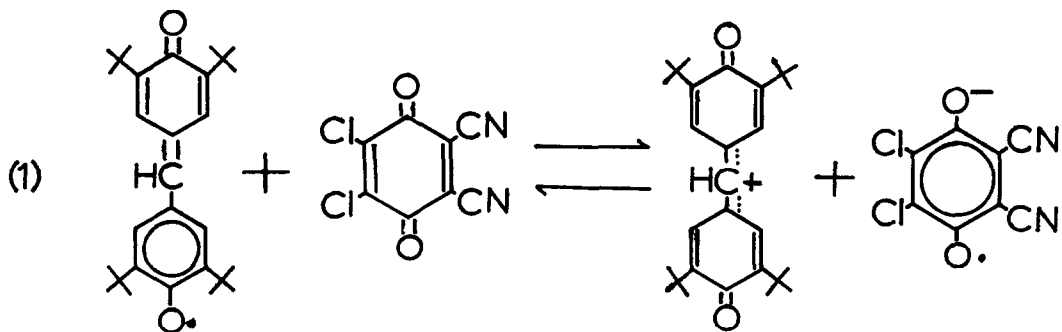
When a 10^{-5} to 10^{-2} M solution of galvinoxyl radical in THF is added under high vacuum to a 0.1 to 1M solution of 2,3-dichloro-4,5-dicyano-4-benzoquinone (DDQ) a large single esr line (line width 1G) appears superimposed upon the ten line esr signal for the galvinoxyl radical. Only the single fast exchange line is observed for DDQ anion radical, due to the rapid exchange of spin with the large excess of neutral molecule. The g factor and the line width for the single line is identical to that for the anion radical of DDQ reduced with

heat of solution, the electron affinity of the DDQ, and the ionization potential of the galvinoxyl radical. Over a small range of temperature, where the dielectric constant of the THF does not vary appreciably, we expect a linear relationship between $\ln K_{eq}$ and $1/RT$. The enthalpy of the reaction is given by a plot of $2 \ln \{ (DDQ^{\cdot-})/h' + (G)/h' - (G)/h \}$ vs. $1/RT$. The slope is the negative of the enthalpy when h is the intensity of the second esr line of the galvinoxyl radical at 25°C, h' is the intensity of this line at temperature T , and (G) represents the concentration of the galvinoxyl at 25°C. As the temperature is lowered, the concentration of the galvinoxyl decreases yielding a linear modified Van't Hoff plot. The enthalpy from the plot is about -2.2 Kcal/mole. The concentration of the DDQ anion radical, even when produced by potassium reduction, decreases with the lowering of the temperature. This indicates that at lower temperatures the anion radical of DDQ forms a diamagnetic species, possibly the dimer dianion. This fact leads to some error in our determination of ΔH , since at lower temperatures, the concentration of the galvinoxyl cation may be greater than that of the DDQ anion radical. The error is minimized by basing the determination of ΔH only upon the concentration dependence of the galvinoxyl radical upon temperature.

The entropy of formation of the complex is found to be ca. -21e.u.. The negative values for ΔH and ΔS suggest large solvation changes are associated with the formation of the complex and are consistent with the formation of ionic species. Addition of hexane to the DDQ galvinoxyl system decreases the dielectric constant of the solvent and, as is expected, drives the equilibrium to the left.

When tetracyanoethylene (TCNE) is added to a solution of galvinoxyl radical in THF, the esr signal for the galvinoxyl radical diminishes and that of the anion radical of TCNE appears. In this case the hyperfine structure for the TCNE anion radical can be observed ($a_N = 1.59G$). The observation of hyperfine coupling in the case of TCNE and not in the case of DDQ is due to the fact that TCNE has a larger electron affinity and only a small excess of neutral TCNE is needed.

potassium metal and containing an equivalent amount of excess neutral molecule. The reaction occurs with the simultaneous diminishing of the galvinoxyl signal and increasing of the DDQ anion radical signal. These results can be explained by equation 1.



If no strong ion pairing is present, the equilibrium constant is given by $K_{eq} = (\text{DDQ}\cdot)^2 / (\text{galvinoxyl})(\text{DDQ})$. By comparing the galvinoxyl and DDQ anion radical esr signal to that of a galvinoxyl spin standard, we have obtained a quantitative fit to this equation over the concentration range described above. The equilibrium constant is $1.2 \pm 0.5 \times 10^{-3}$. The error expressed is the standard deviation. If the reaction proceeds with the formation of an ion pair, the (DDQ) term in the expression for K_{eq} should not be squared. Due to the large error involved in the use of spin standards, we have not been able to rule out the formation of ion pairs on the bases of K_{eq} only. However, the entropy calculated with this assumption is positive, and it is clearly impossible to have a positive entropy for the formation of a charge transfer complex, even an ion pair.

The enthalpy of the reaction consists of three predominant terms: the

Further, the coupling constant for the TCNE anion radical is larger than that for DDQ (0.50G) making it more difficult to time average. Lowering the temperature of this system increases the concentration of the TCNE anion radical and decreases the concentration of the galvinoxyl radical indicating that the enthalpy of formation is negative. Due to the complex overlap of esr lines, the enthalpy was not determined quantitatively.

K_{eq} for the system galvinoxyl radical-DDQ-THF has been determined using commercial grade galvinoxyl radical and using galvinoxyl radical purified by the method of Coppinger, and K_{eq} was found to be independent of the purity of the galvinoxyl radical used. This is evidence that the proposed electron transfer involves the galvinoxyl radical as a donor and not an impurity in it. Further, reactions carried out in the total absence of light led to the same results.

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References

1. a) D.N. Stamires and J. Turkevich, J. Am. Chem. Soc., 85, 2557 (1963).
b) R.S. Mulliken and W.B. Person, "Molecular Complexes: A Lecture and Reprint Volume", Wiley Inc., New York, 1969.
2. a) F.E. Stewart and M. Eisner, Mol. Phys., 12, 173 (1967).
b) D.F. Ilten and M. Calvin, J. Chem. Phys., 42, 3760 (1965).
3. N.H. Kolodny and K.W. Bowers, J. Am. Chem. Soc., 94, 1113 (1972).
4. A.L. Buley and R.O.C. Norman, Proc. of the Chem. Soc., 225 (1964).
5. G.M. Coppinger, J. Am. Chem. Soc., 79, 501 (1957).