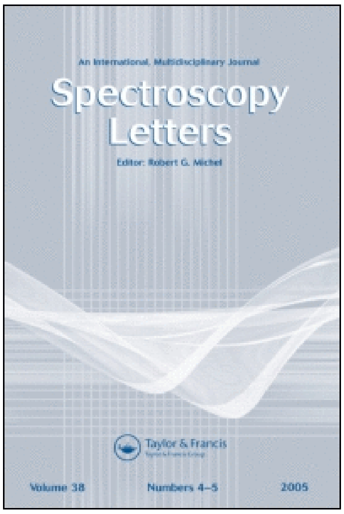

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THE ROLE OF FLUORINE SUBSTITUTED ACETIC ACID IN STABILIZATION OF ORGANOSULFUR CATION RADICALS: A KINETIC E.S.R. STUDY

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Trifluoroacetic acid, the widely used solvolytic agent, is generally acknowledged to be a good solvent in stabilizing organic cations due to its acidity and low nucleophilicity[1]. Although some years ago Dannenberg[2] has carried out INDO calculations on the potential surfaces of such probable interactions between the CF_3 group and the carbenium ion, little experimental evidence of the actual molecular interactions has been known. In our continuing study of the CIDEP (chemically induced dynamic electron polarization) applications to chemistry, we have recently initiated a model charge transfer reaction between benzoquinone cation radical and organosulfur compounds in trifluoroacetic acid[3]. Photochemically induced electron polarization of the benzoquinone cation radical is followed by a well defined secondary polarization transfer in the charge transfer reaction leading to a polarized organosulfur cation radical. One of the interesting observations is that the organosulfur cation radical polarization is the strongest in trifluoroacetic acid solvent. Since trifluoroacetic acid is well known to possess the unique 'property' of stabilizing cation radicals, we wish to report here some e.s.r. experimental evidence which will shed some light on the nature of the molecular interactions between the fluorine substituted acetic acids and thianthrene cation radicals in solution

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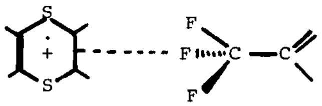
which is responsible for the stabilization of the radicals as observed by kinetic e.s.r. measurements.

A model representing the cation radical - solvent interaction is similar to those proposed by Dannenberg[2] :



It is obvious to us that with the free rotation of the F_3C-C bond, the number of fluorine substitution in the methyl group would determine the averaged degree of interaction and thus the degree of stabilization. Since cation radicals such as the thianthrene is known to decay by self-reaction in trifluoroacetic acid[4], a relative determination of the rate constants in a number of related solvents will serve as an indicator of the degree of stabilization of the cation radicals in those solvents. Furthermore, since thianthrene cation radicals are electron polarized by the CIDEP effects[3], it is possible to estimate T_1 of the thianthrene cation radicals in various selected solvents, namely the three differently fluorine substituted acetic acid. The solvent-radical interaction is expected to affect the values of T_1, thus providing some qualitative evidence for the interaction at the molecular level. It is well recognized in the semiquinone radical systems[5] that the T_1 values increase from hydrocarbon solvent to hydroxylic solvents. The latter solvents can form hydrogen bonding with the semiquinone radicals.

The photochemical reactions of benzoquinone and thianthrene were carried out in three different fluoroacetic acid solvents, trifluoro-, difluoro-, and monofluoro acetic acids. The reactions can be represented by the following scheme[3]:

$$Q^{\dot{+}*} + S \longrightarrow Q + S^{\dot{+}*} \qquad [1]$$

$$S^{\dot{+}*} \longrightarrow S^{\dot{+}} \quad \text{(Spin-lattice relaxation)} \qquad [2]$$

$$2S^{\dot{+}} \xrightarrow{k_3} S^{2+} + S \qquad [3]$$

The self-reaction in [3] is supported by a good second-order kinetic plot of the disappearance of the cation radicals as a function of time, as monitored by e.s.r. The radical concentrations were calibrated against DPPH standard, as well as a fully converted radical ion system using strong oxidizing agents. At 25 °C, the decay of the cation radicals is so slow in trifluoroacetic acid that no e.s.r. measurement of the radical disappearance was significant over the period of hours. In difluoroacetic acid, the averaged k_3 over a range of initial thianthrene concentrations between 5×10^{-3} and 1×10^{-3} has a value of 2×10^{2} l mol^{-1} s^{-1}. In monofluoroacetic acid, the corresponding k_3 has a value of 10^{5} l mol^{-1}s^{-1}. While it is interesting to note that semiquinone radical self-reactions are normally near diffusion-controlled, the self disproportionation of thianthrene cation radicals are definitely not. In the temperature range between 25 and 65 °C, the activation energy associated with the decay in difluoroacetic acid is found to be 28 ± 5 kJ mol^{-1}.

The spin-lattice relaxation of thianthrene cation radicals was monitored by time-resolved CIDEP experiments in all three different solvents at 0 °C. In trifluoroacetic acid, T_1 is 1.5 ± 0.5 μs. In the other two solvents, T_1 was found to be substantially shorter and it was beyond our instrumental time resolution to give a good estimate, although qualitative transient ploarization decay could still be observed.

Both the kinetic e.s.r. and the T_1 experiments provide the experimental evidence of the molecular interactions between the fluorine(s) of the methyl group of the acetic acid and the thianthrene cation radical. The results further establish that the averaged degree of interaction depends upon the number of fluorine(s) in the methyl group.

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