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ELECTRON TRANSFER PROCESSES IN THE REACTION OF PHENOTHIAZINE AND 10-METHYLPHENOTHIAZINE WITH 2,2'-AZOBISISOBUTYRONITRILE

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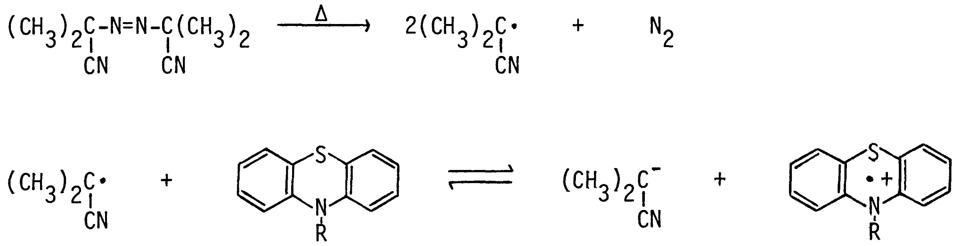
Electron transfer processes in the reaction of phenothiazine and 10-methylphenothiazine with 2,2'-azobisisobutyronitrile have been examined by UV and ESR spectroscopies. The reaction was found to proceed via one electron transfer from phenothiazine derivatives to a cyanoisopropyl radical.

Electron transfer processes involving radical species have been demonstrated for the following reactions: the reaction of oxygen with nicotinamide adenine dinucleotide (NAD),[1)] the oxidation of alkyl radicals with copper (II) acetate and other carboxylates,[2)] the oxidation of a variety of substituted phenyl radicals with the anions of nitroalkanes to yield the corresponding radical anions,[3)] the reaction of a strongly nucleophilic free radical with pyridinium, quinolium, and pyrazinium salts,[4)] and the reduction of alkyl radicals generated in the reaction of alkyl halides with reducing agents such as the aromatic anion radicals.[5)]

We now report spectroscopic and chemical evidences to support that one electron transfer is involved in the reaction of a cyanoisopropyl radical generated by pyrolysis of 2,2'-azobisisobutyronitrile (AIBN) with phenothiazine (**I**) or 10-methylphenothiazine (**II**).



$$(CH_3)_2\underset{CN}{C}\text{-N=N-}\underset{CN}{C}(CH_3)_2 \xrightarrow{\Delta} 2(CH_3)_2\underset{CN}{C}\cdot + N_2$$

R = -H (**I**), -Me (**II**)

A solution of 8×10^{-2} M **I** and 8×10^{-2} and/or 8×10^{-3} M AIBN in acetic acid was placed in an UV cell maintained at 50 and 70°C, and the absorption spectra were recorded. The solution was initially pink in color but became green on standing. As the reaction proceeded the absorption maxima appeared at 638, 517, 498, and 434 nm, which were in fair agreement with those of a cation radical of **I** reported by H. J. Shine.6) The intensities of these bands decreased with time. The formation of the cation radical of **I** was accelerated with increasing molar concentration of AIBN as well as the reaction temperature. Similar results were obtained in the reaction of **II** with AIBN to give characteristic absorption bands of a cation radical of **II**. The ESR spectra of these cation radicals in acetonitrile were observed at 60°C. Hyperfine splitting constants for **I** (a^{N} = 6.90 G, a^{N-H} = 7.05 G) and **II** (a^{N} = 7.29 G, a^{N-Me} = 7.15 G) agreeded with those obtained by several workers.6, 7) It should be noted that no characteristic signals (ESR and UV) of cation radicals of **I** and **II** could be detected in the absence of AIBN.

A mixture of **I** (1.99 g, 10.0 mmol) and AIBN (1.65 g, 10.0 mmol) in acetonitrile (25 ml) was stirred at 70°C for 10 min, and then H_2O was added to the mixture. The mixture was heated for 2 h, then poured into ice-water, and filtered. The filtrate was extracted with benzene. The organic layer gave, upon removal of the solvent, a solid residue which was purified by TLC to yield phenothiazine 5-oxide (**III**): yield 87 mg; mp 255°C (lit.6) 251-253°C). Anal. Calcd for $C_{12}H_9NSO$ (**III**): C, 66.97; H, 4.18; N, 6.51. Found: C, 66.86; H, 4.17; N, 6.41. λmax 272, 303, and 343 nm.6) Formation of phenothiazine 5-oxide also indicates clearly the occurence of cation radical of phenothiazine which arised in the reaction of phenothiazine with AIBN.

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