Effect of Viscosity on the Cage Recombination of 2-Cyano-2-propyl Radicals

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Summary The extent of cage recombination of 2-cyano-2-propyl radicals is dependent on the viscosity of the medium.

GEMINATE recombination of free radicals has been demonstrated for alkoxy-radicals produced from a variety of sources, including peroxyacetates (by thermolysis)[1] and peroxides (by photolysis).[2] It has also been shown that the rates and extents of these cage reactions are sensitive to the bulk viscosity of the medium, although the quantitative relationship between the two has not yet been settled.[3] In many cases the viscosity was varied by varying the solvent, but it is possible that the results are complicated by variable solvent interaction with the radicals.

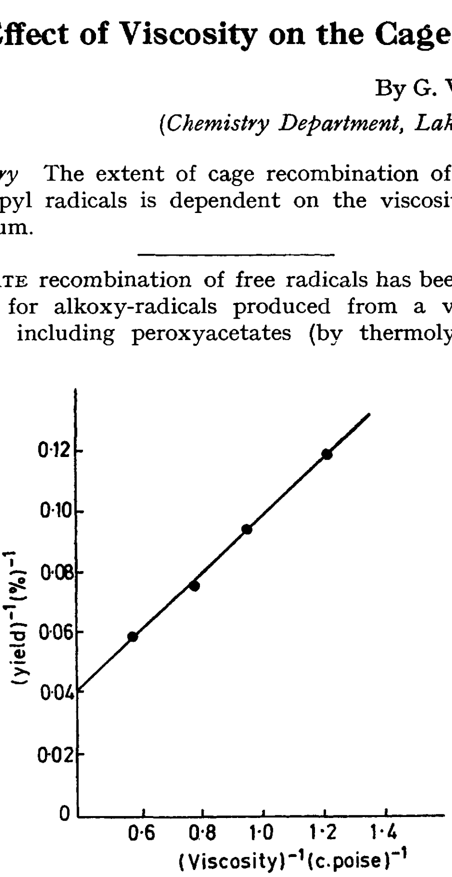

FIGURE. *Reciprocal yield of tetramethylsuccinyldinitrile as a function of the fluidity (viscosity)$^{-1}$ of the solution.*

While studying the photo-decomposition of 2,2′-azo-bis-isobutyronitrile in solutions of polymers, evidence was obtained for a viscosity dependent cage recombination of the 2-cyano-2-propyl radicals, the viscosity being varied by varying the polymer concentration. This system has the advantage of eliminating possible differential radical-solvent interactions. Photolysis was carried out at 313·0 nm in benzene solutions of polystyrene which contained an excess of butanethiol in the presence of which only primary cage recombination of radicals is possible. The azobisisobutyronitrile concentrations and reaction times were identical in each reaction.

Polystyrene was selected since it is known to terminate by combination during its preparation. Polymers which terminate by disproportionation contain double bonds which might be susceptible to attack by the radicals being studied in this work.

The results are shown in the Figure in which the reciprocal yield of cage product, tetramethylsuccinyldinitrile (expressed as a percentage of the theoretical yield, assuming complete decomposition occurs) is plotted as a function of the fluidity ($1/\eta$) of the solution. It can be seen that the yield of cage product increases with increasing viscosity. The data can be correlated by a function of the form,

$$(\text{yield})^{-1} = \alpha + \beta(\eta)^{-1} \quad (\alpha \text{ and } \beta \text{ are constants})$$

which is similar to that established by Noyes.[4]

In support of the present preliminary work, a similar relation has been observed when the viscosity of the above solutions is varied by varying the molecular weight of the polymer.

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[4] R. M. Noyes, *Z. Electrochem.*, 1960, **64**, 153.