Evidence for Dual Mechanism in Poly(vinyl chloride) Degradation

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Summary Poly(vinyl chloride) was found to degrade thermally *via* a dual mechanism—the unimolecular elimination of hydrogen chloride, and a radical chain process, the latter being the predominant pathway at 194 °C.

RECENTLY Gupta and St Pierre[1] proposed a radical chain mechanism for poly(vinyl chloride) degradation with the breaking of an allylic carbon–chloride bond as the initiation step. Evidence for this process was suggested by high activation energies, *ca.* 60 kcal mol^{-1}, for the formation of allylic radicals. This mechanism would, however, also imply that (a) a sufficiently large number of allylic carbon chlorine bonds exist in poly(vinyl chloride) (PVC); and (b) that bond rupture occurs readily at a temperature as low as 150 °C whilst in allyl chloride, a comparable model compound, pyrolysis does not begin below 370 °C.[2]

We now propose an alternative hypothesis; that prior to the radical initiation step, molecular elimination of hydrogen chloride takes place to form olefinic sites. Once a critical number of double bonds is created the chain reaction may proceed concurrently with the molecular reaction. To test this idea we investigated the fully-inhibited degradation *i.e.* in the presence of efficient radical traps. The magnitude of the activation energy for the inhibited reaction can then be used to identify the non-radical chain process; either homolytic bond rupture or elimination of hydrogen chloride.

Degradations were performed on thin films cast from tetrahydrofuran solution. Films were inserted into a perforated Teflon thimble which was placed within a cylindrical Pyrex reactor, heated and controlled electrically. Adequate heat transfer was provided by means of benzene vapour. Prior to each run the reactor was outgassed and on completion the gaseous product was absorbed in water and determined titrimetrically. Percentage dehydrochlorination was calculated from the amount of hydrogen chloride produced and that originally present in the polymer sample, number-average molecular weight 70,000. The polymer used was Geon 101EP, free of additives. Throughout the entire study, the same amounts of PVC, 0·2000 g, were used in each experiment.

Control experiments at 194 °C indicated that the degradation rate was independent of benzene pressure and film thickness, but was accelerated by glass surface, added hydrogen chloride and very markedly by hydrogen bromide. In the early stages the decomposition obeyed first-order kinetics. Hydrogen halide catalysed reactions were found to be first order with respect to each reactant. Activation energy for the degradation in the presence of benzene was $23{\cdot}8 \pm 0{\cdot}4$ kcal mol^{-1} in the range of 172—238 °C. Replacement of benzene with toluene yielded an activation energy of $24{\cdot}2 \pm 0{\cdot}5$ kcal mol^{-1} in the range 173—261 °C. Absence of inhibition in the present experiment contrasts with the liquid phase study of Bamford and Fenton.[3] Failure of toluene to inhibit the degradation indicated that insufficient toluene was contacting the polymer, possibly due to slow diffusion rate into the film. High boiling point compounds with readily abstractable hydrogen atoms were then tested. It was reasoned that once thin films coated with additive were treated above the PVC glass transition temperature chain segmental movement would ensure uniform distribution.

Triphenylmethane (TPM) and hexamethylbenzene (HMB) were chosen as radical traps. At 194 °C both reduced the dehydrochlorination rate at maximum inhibition to about 25 and 33% respectively, of the uninhibited value. The following conditions were used for determination of Arrhenius parameters: TPM-inhibited runs, 2×10^{-3} mol TPM/0·200 g PVC, 177—225 °C; HMB-inhibited runs, 3×10^{-3} mol HMB/0·200 g PVC, 181—226 °C. The Arrhenius parameters for these two reactions were found to be equal within experimental error.

$$\text{TPM, } E = 50{\cdot}1 \pm 0{\cdot}9 \text{ kcal mol}^{-1}, \log A = 15{\cdot}5 \pm 0{\cdot}02$$

$$\text{HMB, } E = 51{\cdot}0 \pm 0{\cdot}8 \text{ kcal mol}^{-1}, \log A = 15{\cdot}5 \pm 0{\cdot}07$$

Magnitude of the activation energies for the inhibited degradation compares favourably with that for molecular elimination of hydrogen chloride from a secondary alkyl chloride such as isopropyl chloride ($E = 50{\cdot}5$, $51{\cdot}1$ kcal mol^{-1},[4] and is significantly smaller than expected for the homolytic breaking of an allylic carbon–chlorine bond (59 kcal mol^{-1}).[4] Pre-exponential factors are about 100 times larger than those expected for the molecular reaction of model compounds. These high values may be rationalised on the basis of increased probability of loss of hydrogen chloride from a polymer chain due to the large number of chlorine atoms available per macromolecule. This explanation is supported by a trend towards higher pre-exponential factors for multi-substituted alkyl chlorides.[4] A high *A* factor may well account for the ability of PVC to undergo elimination at temperatures below those of model compounds.

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[4] A. Maccoll, *Chem. Rev.*, 1969, **69**, 33, and references therein.