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Thermal Decomposition of 4,4'-Azobis(4-Cyanopentanol)

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SUMMARY

Several workers (REED, 1971, 1972, GOLDFEIN, 1975, KARTAVYKH, 1977) have employed the 4.4'-azobis(4-cyanopentanol) (ACP) as the initiator for the radical polymerization of butadiene, isoprene or acrylic monomers. Nevertheless, the decomposition of (ACP) has never been studied, only the rate constant of decomposition (k_d) of (ACP) at 70°C in acetone has been determined.

The present paper reports the kinetics of the thermal decomposition of (ACP): the rate constant of decomposition (k_d) at various temperatures and the activation energy of decomposition are determined in dimethyl sulfoxide.

EXPERIMENTAL

4,4'-azobis(4-cyanopentanol): was prepared as follows by a modification of the procedure outlined by Bamford (1960). 14.3 g of hydrazine sulfate (0.22 mole) are dissolved in 150 ml of water contained in a 3 necked 1 l flask. 22.5 g of 5-hydroxy-2-pentanone are added, followed by slow addition of a solution of 10.8 g sodium cyanide in 100 ml of water. The resulting solution is allowed to stand overnight. The mixture is then cooled in a ice bath and 15% acqueous hydrochloric acid is added until the solution was acidic. Bromine, 32 g is then added very slowly with mechanical stirring at ca. 2°C. The addition should take 5 hours, a yellow coloration appears in the solution at the end. Excess bromine is removed by adding sodium bisulfide. After standing overnight at 2°C the precipitate is filtered off. This precipitate correspond to the insoluble isomer in toluene of the azo compound (mp = 94-96°C). The filtrate is retracted with a mixture of methylene chloride-acetone (2:1).Removal of the organic solvents leave a solid residue which is recrystallized from ethanol by cooling the mixture. The solid isomer , mp = 81-83°C, is so extracted.

Procedure for measuring rates of decomposition

The decomposition of 4,4'-azobis(4-cyanopentanol) was carried out in 45 ml of dimethylsulfoxide in a 50 ml two-necked flask, fitted to a jacketed gas buret. The reaction vessel was immersed in a constant temperature bath controlled to ± 0.1°C. The solvent was deoxygenated with a slow stream of nitrogen for a period of thirty minutes and then allowed a few minutes to obtain thermal equilibrium with the bath. A weighed amount, usually between 0.1 and 0.2 g, of solid azo compound was next introduced into the reaction vessel by momentary removal of the groundglass neck bearing the nitrogen inlet. The flask was then swirled to effect solution and thorough mixing. Timing began with the first introduction of the azo compound. The volume of the nitrogen (V) evolved was measured by means of the gas buret at time intervals which varied with the rate of the reaction being followed volume readings obtained after twenty four hours were treated as V_∞ values in most cases. They agreed well with stoichiometric V_∞ values were used. The natural logarithms of the ratios $V_\infty/V_\infty-V_t$ were calculated and plotted as ordinates vs. the time abscissa.

All these plots revealed apparent induction periods. The slopes or the best straight line through the points so plotted were measured and are the rate constants reported.

RESULTS AND DISCUSSION

4,4'-azobis(4-cyanopentanol) (ACP) exists in two isomeric forms which differ in melting point and solubility characteristics (REED,1971...).The higher melting isomer (94-96°C) possessed a very limited solubility in toluene at ambiant temperature. The low melting isomer (81-83°C) is readily soluble in toluene. Dioxane, DMF, THF, acetonitrile, acetone, isobutanol and dimethylsulfoxide (DMSO) were excellent solvents for all forms of the initiator.

The decomposition rates as measured by nitrogen evolution, on the mixture of the two isomers, appear to be strictly first order after a short induction period. In Fig. 1, plots of $\ln V_\infty/V_\infty-V_t$ are reproduced for (ACP) at five temperatures between 60 and 84°C. The slope of straight lines give the values of the rate constants of decomposition of (ACP) (Table 1)

Table 1 - Effect of temperature on the rate of decomposition of 4,4'-azobis(4-cyanopentanol)

Temperature	60	65	70	78	84
k_d $sec^{-1} x\ 10^{-5}$	1.28	2.43	4.52	11.80	23.56

The value at 70°C is to be compared with the one measured by KARTAVYKH.(1977) who find $k_d = 4.26 \times 10^{-5}$ sec^{-1} in acetone at the same temperature. The little change in rate for (ACP) with different solvents is in accordance with the conclusion of KWEI (1965) and LEWIS (1949) who report that the decomposition of azo compounds is independent of solvent.

Deviations of calculated values of $\text{Ln}\ V_\infty/V_\infty-V_t$ from "true" values at accurately constant temperatures arise chiefly from errors in the measurement of V_t and V_∞ . While errors in V_t unless systematic, merely produce a scatter of the points, an error in V_∞ will produce a deviation from linearity increasing rapidly toward longer times. Our curves exhibited scatter from linearity, but this was not serious. A more serious difficulty was the presence of an apparent "induction period" (see Fig.1) which was reduced but not eliminated by deplacing air from the solvent

Fig. 1 - Decomposition of 4,4'-azobis(4-cyanopentanol) (ACP) in DMSO at 60°C ● , 65°C ○ , 70°C + , 78°C □ , 84°C ∘

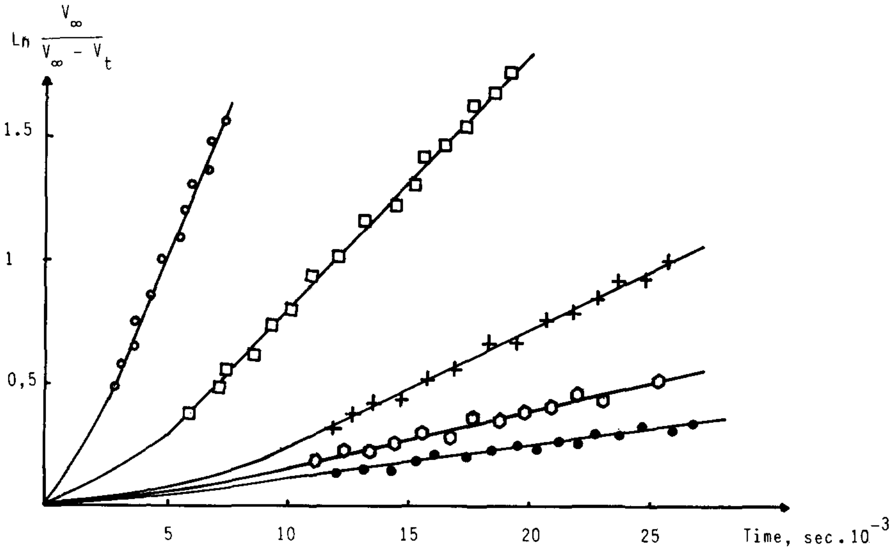
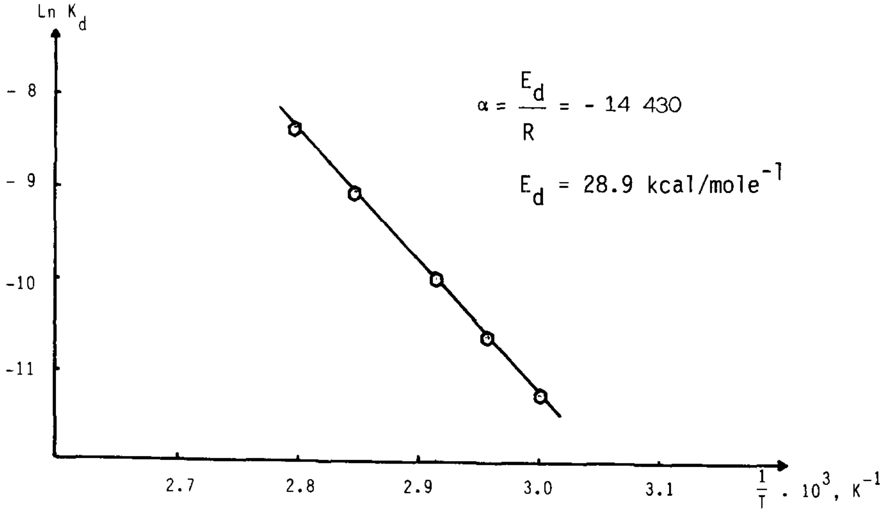


Fig. 2 - Arrhenius plot for the decomposition of 4,4'-azobis(4-cyanopentanol) in DMSO



and the reaction vessel with a stream of nitrogen, before the start of the reaction. This least measure also improved the agreement between the experimental and stoichiometric values of V_∞ . A plausible explanation of induction period is the reaction of oxygen in the solvent and from the gas above it with free radicals formed in the decomposition reaction, thus falsifying the early volume readings. The method used to introduced the sample necessarily admitted some air to reaction vessel; the persistance of the induction period in the experiments in which nitrogen was used is therefore not inconsistent with this explanation. The induction period introduced additional uncertainity in the drawing of the best straigth line through the experimental points by reducing the range of linearity of the $LnV_\infty/V_\infty-V_t$ curves. Furthermore, this curves were smoothed by a linear regression which explained the offset value at the origin.

From the values of k_d (Table 1), the corresponding Arrhenius plot is given in Fig.2. The activation energy of decomposition, Ed, obtained from the slope of the line was 28.9 kcal/mol^{-1}. This result is closed to the activation energy of decomposition usually reported for azo compound as 2,2'-azobis isobutyronitrile (Ed = 29 (TALET-ERBEN,1955) to Ed = 33 (KWEI, 1965), through Ed = 31.3 kcal/mol^{-1} (LEWIS, 1949) or as 4,4'-azobis(4-cyanopentanoic acid) ,Ed = 28 (PRAMANICK, 1981) to Ed = 32 (OVERBERGER, 1970).

CONCLUSION

The decomposition rates of the (ACP) measured by nitrogen evolution were in all temperatures studied first order after a short induction period, probably due to a thermal adjustment after sample addition and to the disappareance of oxygen traces introduced with the sample.

Apparently the solvent did not affect the thermal decomposition of (ACP) in the range studied.

The close agreement between the activation energy of decomposition of (ACP) and others azo compounds would suggest that the electronic effect of the alkyl groups across the C-N=N-C linkage did not affect the decomposition of (ACP).

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