

1157. *Reactions of Macromolecules. Part VII.* Kinetics of the Quaternisation of Poly-(4-vinylpyridine) by n-Butyl Bromide in Tetrahydrothiophen 1,1-Dioxide, Dimethylformamide, and their Mixtures.*

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For the reaction of poly-(4-vinylpyridine) with n-butyl bromide in tetrahydrothiophen 1,1-dioxide, as reported by Coleman and Fuoss,¹ the specific second-order rate† falls as reaction proceeds. In a series of mixtures of tetrahydrothiophen 1,1-dioxide with increasing proportions of dimethylformamide, this deceleration is lessened, and in dimethylformamide the reaction closely follows second-order kinetics (Figs. 1 and 2).

In a kinetic study of the quaternisation of poly-(4-dimethylaminostyrene) by methyl iodide in dimethylformamide at 0°,² we observed that the specific second-order rate† alters little during the first 20—25% of reaction, but thereafter falls; when 50% quaternisation has occurred, it has decreased to 60% of the initial value.

The fall in rate was ascribed to the accumulation of positive charge on the macromolecule as the quaternary ammonium groups are formed. A similar fall in rate had been observed by Coleman and Fuoss¹ for the quaternisation of poly-(4-vinylpyridine) by n-butyl bromide

* Part VI, C. L. Arcus and R. J. Still, *J.*, 1964, 4340.

† *I.e.*, the "instantaneous" second-order rate constant.

¹ B. D. Coleman and R. M. Fuoss, *J. Amer. Chem. Soc.*, 1955, **77**, 5472.

in tetrahydrothiophen 1,1-dioxide. In an attempt to elucidate the deceleration effect, we have carried out rate determinations on this reaction in this solvent at 75°, and extended the measurements to dimethylformamide and its mixtures with the dioxide.

EXPERIMENTAL

Ethanol refers to the 96% aqueous alcohol.

Dimethylformamide was purified as described earlier.² Tetrahydrothiophen 1,1-dioxide (for which we thank the Shell Chemical Company) was distilled. The first 20%, which carried over the trace of water present, was rejected; the fraction collected had b. p. 116°/2 mm., n_D^{40} 1.4778. Subjected to gas-liquid chromatography, by means of 10% silicone on 109-125 Celite at 150°, it gave only a single peak. Solvent mixtures were kept under nitrogen, and used within 4 days of preparation.

n-Butyl bromide was dried over sodium sulphate and distilled; it had b. p. 102°, n_D^{25} 1.4373. Timmermans³ records b. p. 102°, n_D^{25} 1.4373. Pyridine was dried over potassium hydroxide, then distilled under nitrogen; it had b. p. 114°, n_D^{25} 1.5058. 4-Vinylpyridine was similarly dried and distilled; the fraction of b. p. 64-65°/17 mm. was collected. Fitzgerald and Fuoss⁴ record b. p. 68°/18 mm. These compounds were subjected to gas-liquid chromatography; 10% Carbowax 1000 on 109-125 Celite was used at 50°, 75°, and 125° respectively. Each chromatogram showed essentially a single peak; no impurities were apparent in the n-butyl bromide and pyridine. The 4-vinylpyridine had present three impurities totalling less than 2%.

$\alpha\alpha'$ -Azobisobutyronitrile (0.205 g.) was dissolved in 4-vinylpyridine (49.4 g.) which was then sealed under nitrogen in a number of thin-walled soft glass tubes and kept for 24 hr. at 70°. The very viscous product dissolved in t-butyl alcohol (500 ml.) in the course of 3 days' stirring. To the filtered solution, benzene (1 l.) was added slowly with high-speed stirring. The supernatant liquid was decanted from the precipitate, a gel, which was thrice washed with benzene (100 ml. portions) then dissolved in t-butyl alcohol (160 ml.). This solution was subjected to freeze-drying by Fitzgerald and Fuoss's procedure,⁴ and yielded white, porous, friable poly-(4-vinylpyridine) (17 g.); it was dried to constant weight at 56°/0.2 mm. (Found: N, 13.45, 13.35. Calc. for C₇H₇N: N, 13.3%). The limiting viscosity number of the polymer, in solution in ethanol at 25°, was determined by the method described earlier;² it had $[\eta]$ 0.876, whence^{5,6} it had M , 163,000.

Pyridine (8 ml.), n-butyl bromide (17.5 ml.), and ethanol (10 ml.) were heated under reflux for 15 hr. The solution was concentrated, then chilled in ice. 1-n-Butylpyridinium bromide crystallised; it was collected, washed with, then crystallised from, dry acetone, and dried at room temperature at 0.1 mm. It had m. p. 105-105.5° (Found: Br, 37.15. Calc. for C₉H₁₄BrN: Br, 37.0%).

A solution of poly-(4-vinylpyridine) (2.6 g.) and n-butyl bromide (21 g.) in nitromethane (60 ml.) was kept at 60° for 4 days. The nitromethane was removed under reduced pressure, and the product dissolved in ethanol (70 ml.). The filtered solution was added dropwise with high-speed stirring to dioxan (750 ml.). The precipitated poly-(1-n-butyl-4-vinylpyridinium bromide) was collected, washed with dioxan (200 ml.), and dried at 56°/0.1 mm. (Found: Br, 33.05, 33.1. Calc. for C₁₁H₁₆NBr: Br, 33.05%).

Rate-determination Procedure.—In each run there were used n-butyl bromide (6.80 mequiv.) and tertiary amine (3.40 mequiv.). The method was as described for the methyl iodide-poly-(4-dimethylaminostyrene) measurements,^{2*} except that: the polymer was dissolved on the preceding day; the solution was brought to 25.0 ml. at 75° ± 0.01°, the temperature of reaction; with bromide ion, the change in potential at the titration end-product is ~ 80 mv.

A slow reaction occurs between n-butyl bromide and dimethylformamide. By means of runs in the absence of amine, the quaternisation runs were corrected for bromide ion formed by reaction with solvent. For the polymer in dimethylformamide, the correction amounted to 10% of the

* It is there stated that in each run methyl iodide (0.2720 equiv.) and tertiary amine (0.1360 equiv.) were used. These numbers are in fact the normalities of the reactants in the final solution; the quantities per run were one-fortieth of the above. The rate constants are recorded correctly.

² C. L. Arcus and W. A. Hall, *J.*, 1963, 4199.

³ J. Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York etc., 1950, p. 265.

⁴ E. B. Fitzgerald and R. M. Fuoss, *Ind. Eng. Chem.*, 1950, 42, 1603.

⁵ J. B. Berkowitz, M. Yamin, and R. M. Fuoss, *J. Polymer Sci.*, 1958, 28, 69.

⁶ R. M. Fuoss, M. Watanabe, and B. D. Coleman, *J. Polymer Sci.*, 1960, 38, 5.

titre at 9 hr. Corrections, progressively smaller with increase in the proportion of the dioxide, were similarly applied to the runs in dimethylformamide-tetrahydrothiophen 1,1-dioxide mixtures. There was no reaction between *n*-butyl bromide and tetrahydrothiophen 1,1-dioxide.

RESULTS AND DISCUSSION

Representative examples of runs are shown in Fig. 1.

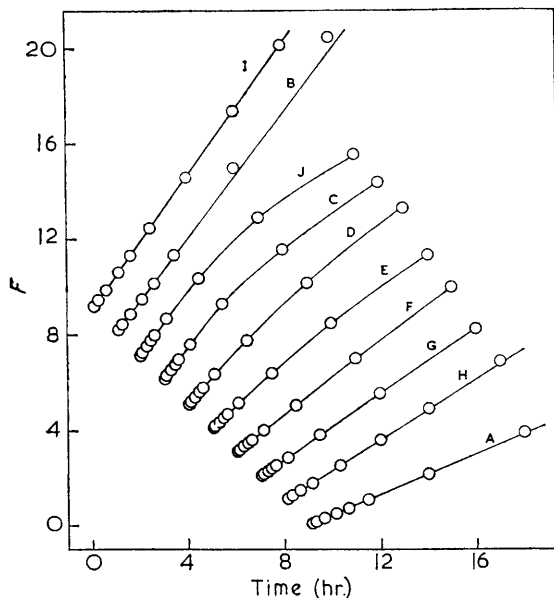


FIG. 1. Reaction with *n*-butyl bromide at 75°: A, B, pyridine in dimethylformamide and in tetrahydrothiophen 1,1-dioxide; C—H, poly-(4-vinylpyridine) in tetrahydrothiophen 1,1-dioxide, in its mixtures with dimethylformamide in weight ratios 80:20, 60:40, 40:60, 20:80, and in dimethylformamide; I, pyridine in tetrahydrothiophen 1,1-dioxide in the presence of 0.81 molecular proportion of 1-*n*-butylpyridinium bromide; J, poly-(4-vinylpyridine) in tetrahydrothiophen 1,1-dioxide in the presence of 0.96 molecular proportion of poly-(1-*n*-butyl-4-vinylpyridinium bromide). The origin has been displaced successively by 1 unit of the ordinate from right to left, and 1 hr. of the abscissa from left to right. (*F*) denotes

$$[\log_e a(b-x)/b(a-x)]/(b-a).$$

The plot of the integral second-order expression against time is linear for the quaternisation of pyridine in dimethylformamide, and for the greater part of the quaternisation in tetrahydrothiophen 1,1-dioxide; in this solvent, at 75% reaction (penultimate point) and beyond, there becomes apparent an increase in rate-constant which is ascribed to a salt effect (below) of the accumulating 1-*n*-butylpyridinium bromide. The plot for the quaternisation of poly-(4-vinylpyridine) in tetrahydrothiophen 1,1-dioxide is linear at first and then, as found by Coleman and Fuoss,¹ becomes concave towards the abscissa. For the tetrahydrothiophen 1,1-dioxide-dimethylformamide mixtures, the initial rate-constant and the deceleration become less as the proportion of dimethylformamide is increased until, in this solvent, there is no appreciable deviation from the second-order kinetic equation.

Values for the second-order constant (*k*) are recorded in the Table: those for pyridine,

Reaction with *n*-butyl bromide at 75°.

Amine	Solvent	<i>k</i> (10 ⁻³ l. mole ⁻¹ min. ⁻¹)	
		Individual runs	Average
Pyridine	Dimethylformamide	7.2, 7.2	7.2
	Tetrahydrothiophen 1,1-dioxide (TD) TD containing 1- <i>n</i> -butylpyridinium bromide	21.9, 21.9	21.9
Poly-(4-vinylpyridine)	Dimethylformamide	22.9, 23.1	23.0
	DMF 80 TD 20	10.7, 10.8, 10.7, 10.7	10.7
	DMF 80 TD 20	12.2, 12.1	12.2
	DMF 60 TD 40	14.2, 14.2	14.2
	DMF 40 TD 60	16.6, 16.5	16.6
	DMF 20 TD 80	20.2, 20.0	20.1
	Tetrahydrothiophen 1,1-dioxide TD containing poly-(1- <i>n</i> -butyl-4- vinylpyridinium bromide)	24.0, 23.8, 23.8, 23.8	23.8
		25.0, 25.0	25.0

and that for poly-(4-vinylpyridine) in dimethylformamide, hold substantially throughout the runs; those for the polymer in tetrahydrothiophen 1,1-dioxide and its mixtures are derived from straight lines drawn through large-scale plots of the first, substantially linear, sections. These rate-constants are considered to be those for the pyridine groups attached to the macromolecule before the incidence of the perturbing factor due to accumulating positive charge.

The rate constants for the quaternisation of pyridine and poly-(4-vinylpyridine) in tetrahydrothiophen 1,1-dioxide (dielectric constant 42.0 at 50°¹) are higher than the corresponding values for the reactions in dimethylformamide (dielectric constant 36.7 at 25°.⁷) These results accord with the finding of Menshutkin⁸ and subsequent workers⁹ for non-polymeric amines: that quaternisation is faster the higher the dielectric constant of the solvent.

In order to ascertain whether the age of the solution is relevant to the deceleration observed with poly-(4-vinylpyridine) in tetrahydrothiophen 1,1-dioxide, two solutions (third and fourth of the Table) were kept for 3 days at 75° before kinetic measurements were made. The course of reaction was not altered by this treatment.

It appeared possible that the deceleration might be a salt effect exerted by the polymeric quaternary ammonium bromide as a solute, rather than an effect operating within the volume defined by the individual macromolecule and its counter-ion layer. Accordingly, the rates of quaternisation of pyridine and of poly-(4-vinylpyridine) in tetrahydrothiophen 1,1-dioxide were measured in the presence of, respectively, 1-n-butylpyridinium bromide and poly-(1-n-butyl-4-vinylpyridinium bromide). For pyridine, the initial rate increased by 5%, and second-order kinetics were closely followed throughout the run. This result and that for the reaction without added 1-n-butylpyridinium bromide are consistent with the exertion of a small accelerative salt effect by this compound. For poly-(4-vinylpyridine), the initial rate increased by 5% but there was no other appreciable alteration in the course of the reaction, whence deceleration is not due to a salt effect.

For the kinetic runs with poly-(4-vinylpyridine) in tetrahydrothiophen 1,1-dioxide and its mixtures with dimethylformamide, the times for successive tenths of the reaction were calculated, and the corresponding values of dx/dt obtained from the plot of x against t . The specific reaction rate is then given by $(dx/dt)/(a-x)(b-x)$. Plots of these values (the averages of those of duplicate runs) against percentage reaction are shown in Fig. 2. The initial rate constants, derived from plots of the integrated second-order expression, are shown as broken horizontal lines. The specific reaction rate for quaternisation in tetrahydrothiophen 1,1-dioxide alters little during the first part of the reaction, then falls fairly sharply to a region in which the slope is at first less, then increases. When 70% reaction has taken place, the specific rate has fallen to 63% of the initial value. These trends are seen to lesser extents in the specific rates for mixtures increasingly rich in dimethylformamide until, in that solvent, there is no deceleration.

After having determined the relationships of specific rate to extent of reaction and to solvent composition, we considered a number of apparent explanations of these relationships, but we are unable to put forward a theoretical treatment. We therefore confine ourselves to some comments on Coleman and Fuoss's discussion.¹ These authors first considered the possibility that the $-I$ effect of a pyridinium group might be relayed through the main chain, and render the electrons of an adjacent pyridine group less available for reaction with alkyl halide. They concluded that relay through three aliphatic carbon atoms is unlikely to be effective. The disappearance of the effect when tetrahydrothiophen 1,1-dioxide is replaced by dimethylformamide makes it unlikely that deceleration is dependent on relay through the main chain.

⁷ G. R. Leader and J. F. Gormley, *J. Amer. Chem. Soc.*, 1951, **73**, 5731.

⁸ N. Menshutkin, *Z. phys. Chem.*, 1890, **5**, 589.

⁹ S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, 1941, pp. 414—423.

As modes of action which may be effective, Coleman and Fuoss put forward electrostriction of the solvent by the field of the quaternised nitrogen atoms, and two suggestions concerning the transition state: that the charge on a pyridinium group might (i) orientate an approaching dipolar molecule of butyl bromide into an unfavourable position for reaction

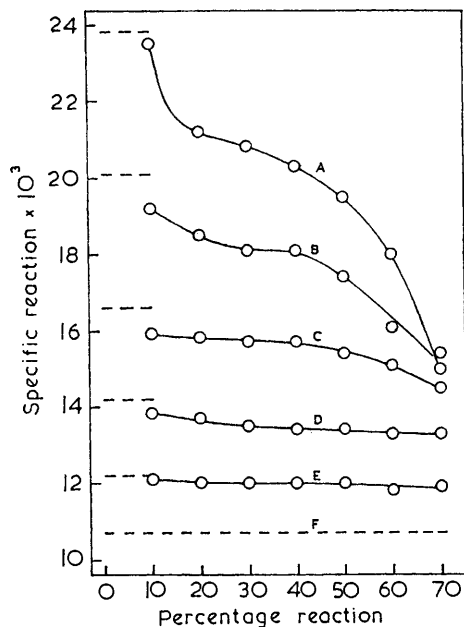


FIG. 2. Reaction of poly-(4-vinylpyridine) with *n*-butyl bromide at 75°. Specific reaction rate $\times 10^3$ versus percentage reaction in: A, tetrahydrothiophen 1,1-dioxide; B—E, its mixtures with dimethylformamide in weight-ratios 80:20, 60:40, 40:60, 20:80; F, dimethylformamide.

with a neighbouring pyridine group, and (ii) stabilise the transition state so that decomposition into the quaternary salt becomes less probable. Whichever of these (or another) mode of action proves to be effective in causing deceleration, it must, in view of the present results, be operative in tetrahydrothiophen 1,1-dioxide and inoperative in dimethylformamide.

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