and equation of Halverstadt and Kumler[27]

$$p_{20} = \frac{3\alpha\nu_1}{(\epsilon_1 + 2)^2} + \frac{(\nu_1 + \beta)(\epsilon_1 - 1)}{(\epsilon_1 + 2)}$$

$$P_{20} = p_{20}M \qquad M = \text{mol. wt.}$$

$$\mu = 0.01281\sqrt{(P_{20} - P\epsilon)T}$$

The plots of ϵ_{12} *versus* ω_2 and γ_{12} *versus* ω_2 were straight lines within the limits of experimental error. The values of ϵ_1 and γ_1 were obtained by the method of least squares. The standard errors in the dipole moments were calculated from the equation

$$\delta_\mu = 0.0046\frac{M}{\mu}\delta_\alpha{}^{28}$$

and the standard error in α. $\delta\alpha$, from the equation[28,29]

$$\delta_\alpha = \pm\left[\frac{n}{n-2}\left(\frac{\Sigma(\epsilon_1 - \epsilon_{12})^2}{n\Sigma(\omega_2)^2 - (\Sigma\omega_2)^2}\right)\right]^{1/2}$$

The errors from scatter of the points for specific volume do not need to be considered since even large errors in β produce only very small errors in the dipole moment.[30]

Diacetamide was prepared by acetylation of acetamide with acetic anhydride in the presence of ammonium chloride.[31] It was recrystallized several times from CCl_4 (m.p. 81°).

Acknowledgment.—We wish to thank Dr. H. K. Hall, Jr., of du Pont[32] for providing N-methylformamide and N-methyldiacetamide. Gas chromatograpy and n.m.r. showed the original sample of N-methyldiformamide had a small amount of impurity, probably N-methyldiacetamide. N-Methyldiformamide was synthesized by the method of Ray and Ogg[17] and found to contain the same impurity. Purification was effected by gas chromatography using a preparative Apiezon column on an Aerograph model A110-C. All work reported on N-methyldiformamide was done on the purified compound. Dimethylformamide was Eastman Kodak Co., purified by shaking with solid potassium hydroxide, then lime, and distilled.[33]

We wish to thank Mr. M. K. Hrenoff of the Spectrographic Laboratory for all infrared and ultraviolet studies. Infrared spectra were run on Perkin–Elmer model 21 and ultraviolet spectra were run on Cary model 11. Portions of this study were aided by Public Health Grant CY-3211 (C4).

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[27] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2933 (1942).

[28] Private communication, E. W. Randall and Roger Rabb.

[29] R. J. W. Le Fevre, *J. Chem. Soc.*, 404 (1953).

[30] K. B. Everard, R. A. W. Hill and L. E. Sutton, *Trans. Faraday Soc.*, **46**, 417 (1950).

[31] D. Davidson and M. Karten, *J. Am. Chem. Soc.*, **78**, 1068 (1956).

[32] H. K. Hall, Jr., M. K. Brandt and R. M. Mason, *J. Am. Chem. Soc.*, **80**, 6424 (1958).

[33] G. Leader and J. F. Gormley, *ibid.*, **73**, 5731 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNA.]

Polymerization and Copolymerization of N-Vinylpyridinium Salts

BY IRL N. DULING[1] AND CHARLES C. PRICE

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Several new salts of the N-vinylpyridinium ion have been prepared and their physical and chemical properties briefly described. The salts were found to polymerize or copolymerize with both ionizing radiation and free radical initiation. From the copolymerizations it was calculated that $Q = 0.31–1.9$, $e = +1.7–2.4$. It is suggested that the uncertainty in these values may be explained by variation of the separation between radical and ion due to electrical repulsions in the transition state. The existence of resonance interactions between the pyridinium ring and the vinyl group was established by observation of tritium exchange in the rearrangement of N-allylpyridinium salts to N-propenylpyridinium salts.

Introduction

Simple unsubstituted N-vinylpyridinium salts (I) have been reported only twice,[2a,b] and in neither case were any except the most obvious physical properties mentioned. Substituted salts (II) have been extensively investigated,[3–5] but principally with physiological objectives in mind. This paper reports the preparation and properties of several new N-vinylpyridinium salts. The principal portion, however, reports our investigation of the homopolymerization and copolymerization of these salts.

Gillis[6] attempted to copolymerize styrene and methyl methacrylate with vinyltrimethylammonium salts and vinyldimethylsulfonium salts without success. This result can be attributed to a lack of resonance stabilization of the radical derived from these monomers, although it may also be due to electrostatic repulsions. In this regard, it is interesting to note that, although N-allylammonium salts have been polymerized,[7] there are no reported polymerizations of vinyl compounds which carry an electrostatic charge α to the carbon–carbon double bond. It seemed interesting, therefore, to investigate an example in which resonance stabilization of the radical derived from the monomer was possible but which retained the electrostatic charge adjacent to the vinyl group. N-Vinylpyridinium salts provide such a case.

Experimental

N-Vinylpyridinium Fluoroborate.—A solution of 18.8 g. (0.1 mole) of 1,2-dibromoethane in 20 ml. of absolute alcohol was refluxed while 7.9 g. (0.1 mole) of pyridine was added dropwise during 6 hours. After refluxing an additional hour and standing overnight, the precipitated 1,2-(N,N-dipyridinium)-ethane bromide was filtered out and the filtrate evaporated to dryness under vacuum. Drying over phosphorus pentoxide gave 4.9 g. (56%) of crude **N-(2-bromoethyl)-pyridinium bromide**. Recrystallization from absolute ethanol yielded colorless hygroscopic needles, m.p. 126–128° (lit.[2] 100–103°). *Anal.* Calcd. for $C_{13}H_{11}N_4O_7Br$: C, 37.61; H, 2.67; N, 13.49; Br, 19.25. Found: C, 37.76; H, 2.86; N, 12.83; Br, 19.38.

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[1] Sun Oil Co. Fellow, 1959–1961.

[2] (a) F. Cappolla, *Gazz. chim. ital.*, **15**, 333 (1885); (b) E. Schmidt. *Arch. Pharm.*, **251**, 183 (1913).

[3] P. Pfeiffer and A. Longenberg, *Ber.*, **43**, 2935 (1910).

[4] L. C. King and W. B. Brownell, *J. Am. Chem. Soc.*, **72**, 2507 (1950).

[5] R. Kröhnke, *Angew. Chem.*, **65**, 605 (1953).

[6] R. G. Gillis, Ph.D. Thesis, University of Notre Dame, 1952.

[7] G. B. Butler and R. L. Bunch, *J. Am. Chem. Soc.*, **71**, 3120 (1949); D. S. Trifan and J. J. Hoglen, *ibid.*, **83**, 2021 (1961).

Picrate, m.p. 125–127° (lit.[2] 128°). **Perchlorate**, m.p. 89–91°. *Anal.* Calcd. for $C_7H_9NBrClO_4$: C, 29.39; H, 3.17; N, 4.89; Cl + Br(as Cl), 24.75. Found: C, 29.34; H, 3.22; N, 4.55; Cl + Br (as Cl), 24.18. **Chloroplatinate**, m.p. 227–228° dec. (lit.[2] 220–221° dec.)

To 44.4 g. (0.166 mole) of crude N-(2-bromoethyl)-pyridinium bromide in 100 ml. of water was added 0.166 mole of moist silver oxide, freshly prepared from 27.2 g. of silver nitrate and 6.40 g. of sodium hydroxide. After stirring vigorously for 3 min., the mixture was adjusted to *p*H 7 with aqueous hydrobromic acid. Aqueous silver fluoroborate was added until no more silver bromide precipitated and the mixture was filtered. The filtrate, on evaporation to dryness, gave 15.6 g. (46%) of crude **N-vinylpyridinium fluoroborate**.

Repeated crystallization from ethanol gave long colorless needles, m.p. 75.5–76.5°. *Anal.* Calcd. for $C_7H_8NBF_4$: C, 43.57; H, 4.18; N, 7.26; F, 39.34. Found: C, 43.26; H, 4.26; N, 7.13; F, 39.02.

Perchlorate, m.p. 95.5–97.5°. *Anal.* Calcd. for $C_7H_8NClO_4$: C, 40.80; H, 3.93; N, 6.82; Cl, 17.25. Found: C, 40.72; H, 4.04; N, 6.65; Cl, 17.07. **Chloroplatinate**, m.p. 211–213° dec. (lit.[2] 193° dec.). *Anal.* Calcd. for $C_{14}H_{16}N_2Cl_6Pt$: C, 27.11; H, 2.60; Pt, 31.48. Found: C, 27.36; H, 2.59; Pt, 31.40.

Hydrogenation of N-vinylpyridinium perchlorate was carried out in a semi-micro apparatus using 0.2081 g. of the perchlorate and 0.0229 g. of platinum oxide. The sample consumed 103.6 ml. of hydrogen in 3 hours at 25° and 760 mm., compared with 100.7 ml. calculated for 4 moles of hydrogen. On a larger scale, 2.05 g. (0.01 mole) of N-vinylpyridinium perchlorate was hydrogenated using 0.227 g. of platinum oxide in 100 ml. of 90% ethanol and 45 p.s.i. hydrogen in a Parr apparatus. The product was recovered as the picrate, m.p. 168–170° (lit.[8] m.p. for N-ethylpiperidinium picrate, 168°). The infrared spectra agreed with that of an authentic sample of N-ethylpiperidinium bromide.

Reaction with Thiosulfate Ion.—N-Vinylpyridinium perchlorate (0.1868 g.) was dissolved in 50 ml. of water, and 15.0 ml. of 0.1000 *N* sodium thiosulfate solution was added. After heating for 15 min. on a steam-bath, back titration with standard iodine solution showed no consumption of thiosulfate ion. Again, 14.9 ml. of thiosulfate solution was added to 0.195 g. of the salt in 50 ml. of water and, after standing 68 hours at room temperature, back titration indicated 22.9% addition to the N-vinylpyridinium perchlorate.

Addition of Bromine to N-Vinylpyridinium Perchlorate.—Small samples of the salt (0.01–0.02 g.) were dissolved in 5 ml. of water and 10 ml. of a 0.0139 *N* bromine solution in glacial acetic acid was added. After about 5 min. at room temperature, back titration with thiosulfate indicated no addition of bromine.

Polymerization with γ-Irradiation.—The dry crystalline salts were sealed in ampules at 10^{-4} mm. and exposed to a Co^{60} source yielding 500,000 rep./hr. for varying periods of time at approximately 50°. In a typical experiment, N-vinylpyridinium fluoborate, m.p. 75.5–76.5°, after receiving 24×10^6 rep., melted at 195–215°. The irradiated crystals, after trituration with methanol to remove monomer, gave 86% polymer.

Anal. Calcd. for $(C_7H_8NBF_4)$: C, 43.57; H, 4.18; N, 7.28; F, 39.34. Found: C, 43.43; H, 4.52; N, 7.07; F, 39.10.

Polymerization in solution was carried out in the same manner. Ampules containing the solutions were frozen in liquid nitrogen, evacuated, degassed by repeated freezing and thawing, and finally sealed at 10^{-4} mm. After exposure of radiation the tubes were opened and the polymer recovered. Exposure of 0.5 *M* solutions of either the fluoborate salts to 24×10^6 rep. yielded approximately 40% polymer when water or dimethylformamide was the solvent but no polymer in nitromethane solution. The polymer was soluble in hot water but precipitated on cooling. It turned red on treatment with base. The color disappeared immediately on acidification and slowly on standing in base.

Free Radical Polymerization and Copolymerization.—The monomers were weighed out into ampules and azobis-(isobutyronitrile) added in solution in the solvent. The ampules were degassed by freezing and thawing and sealed under vacuum at 10^{-4} mm. Acetic acid (90%) and γ-butyrolactone were found to be the best solvents for the copolymerizations. After heating for 1–24 hours in an oil-bath (both 60° and 80° were used) the tubes were opened and the polymer recovered by precipitation with methanol.

The copolymers were submitted to elemental analysis and the reactivity ratios were calculated by both the Fineman–Ross[9] and intersection techniques.[10]

X-Ray Diffraction Patterns of N-Vinylpyridinium Salts and Polymers.—The finely powdered monomer or polymer was packed into a glass capillary of 0.05 mm. wall thickness and exposed in a Debye–Sherrer camera to copper Kα radiation at 1.5405 Å. for approximately 4 hours.

Viscosities of polymers were obtained with a Ubbelohde type viscometer which gave a flow time for distilled water at 30.00 ± 0.01° of 107.55 sec. The points were taken by successive dilutions of the original concentration.

Preparation of N-Allylpyridinium Perchlorate.—Allyl bromide was added to an excess of pyridine and the crystals collected and washed with anhydrous ether. The bromide was converted to the perchlorate with aqueous silver perchlorate solution. Recrystallization from methanol–ethanol gave long colorless needles, m.p. 69–71°. *Anal.* Calcd. for $C_8H_{10}NClO_4$: C, 43.90; H, 4.45; N, 6.41. Found: C, 43.75; H, 4.59; N, 6.38.

Tritium Exchange of N-Allylpyridinium Perchlorate.—N-Allylpyridinium perchlorate (0.2375 g., 0.00115 mole) was dissolved in 25 ml. of tritiated water which counted at 2.5×10^8 decomp./min./ml. The solution stood for 7 days at room temperature and the salt was recovered by freeze-drying. Drying was completed under vacuum over phosphorus pentoxide and the salt was counted in 90% toluene–10% ethanol using 3,5-diphenyloxazole and biphenoxazoylbenzene as fluors. Counting was done on a Packard Tricarb liquid scintillation counter. There was no exchange of tritium.

In another experiment, 0.263 g. (0.00127 mole) of the salt was dissolved in 18.7 ml. of tritiated water which counted at 1.5×10^8 decomp./min./ml. Pyrrolidine (0.0412 g., 0.00058 mole) was added and the solution was allowed to stand for 6 days at room temperature. The salt was recovered and counted as before. Exchange of 4.0 hydrogen atoms had occurred (see Table V).

Ultraviolet spectra were taken on a Process and Instruments model RS3 and the results are summarized in Table IV. **Infrared spectra** were obtained on a Beckman model 21 using chloride optics. The major features for some of the compounds are

Compound	Phase	Absorption maxima, μ[a]
N-(2-Bromoethyl)-pyridinium perchlorate	KBr	3.18*w, 3.28m, 3.35*m, 3.48*w, 6.11s. 6.32w, 6.71s, 6.40w, 6.48w, 7.26w. 7.37w, 7.60w, 7.90m, 8.13m. 8.72v.s., 9.15v.s., 10.55w, 10.63w, 11.25v.s., 12.92s. 14.20s
N-Vinylpyridinium perchlorate	KBr	3.21m, 3.28m. 3.31*m, 6.05m, 6.13s, 6.35w, 6.67m, 6.76s, 7.05m, 7.50w, 7.87m, 8.35m. 8.30*s, 9.15v.s., 9.80*m. 10.39wm, 10.55m, 10.70m, 12.60s, 14.20m, 15.20m
Poly-(N-vinyl)-pyridinium perchlorate	KBr	3.18*w, 3.24*w. 3.33m, 3.40*w, 3.49*w, 6.12s, 6.32w, 6.65s. 6.70s. 6.85w, 6.90w, 6.95w, 7.28w, 7.61m, 8.18m. 8.36m. 8.78v.s., 9.15v.s.. 9.75m, 10.10w, 10.35w, 10.63w, 12.40w, 12.80s, 14.12*s. 14.22s

[a] Asterisk indicates shoulders.

All **melting points** were measured in a Thomas–Hoover melting point apparatus using a calibrated thermometer. **Microanalyses** were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.; Micro-Tech Laboratories, Skokie, Ill.; Midwest Microlab, Indianapolis, Ind.; and Micro-Analysis Inc., Wilmington, Del.

Discussion

N-Vinylpyridinium salts have been prepared by dehydrohalogenation of N-(2-bromoethyl)-pyridinium bromide with moist silver oxide and subsequent metathesis with the appropriate silver salt

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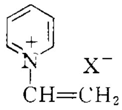
[8] R. D. Closson, J. P. Napolitano, G. G. Ecke and A. J. Kolka, *J. Org. Chem.*, **22**, 646 (1957).

[9] M. Fineman and S. D. Ross, *J. Polymer Sci.*, **5**, 269 (1950).

[10] F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).

or acid. The reaction was found to be complete in three minutes at room temperature in contrast to the "several hours on a steam-bath" reported in the literature. The perchlorate and fluorborate salts were found to decolorize permanganate rapidly, but they did not add bromin eunder the conditions tried. They hydrogenated quantitatively consuming four moles of hydrogen without isomerization or ring cleavage to yield N-ethylpiperidinium salts.

The infrared and ultraviolet spectra, the reaction with permanganate and especially the hydrogenation to N-ethylpiperidinium salts firmly establish the structure of the N-vinylpyridinium salts as shown (I). Even the failure to brominate would be expected since Roche and Price[11] have shown that the more positive the *e*-value, the less is the tendency to add bromine, because as is known, the attacking species in non-radical brominations is electrophilic.



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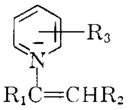
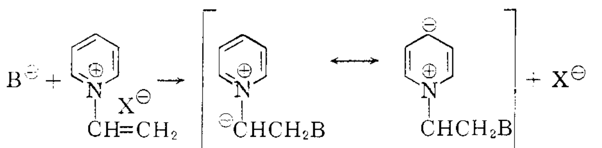


II

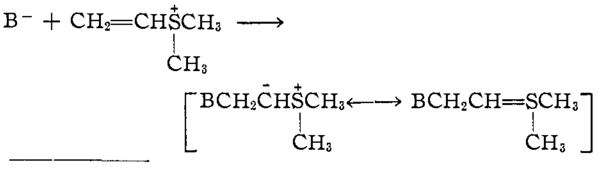
R_1 = H, COOH
R_2 = H, COOH, C_6H_5, thienyl, etc.
R_3 = H, CH_3, etc.



III

The salts were stable to acids but the electron-withdrawing effect of the vinyl group sensitizes the pyridinium ring to nucleophilic attack and solutions of the salts in dilute base slowly (12 hours) precipitated a dark red insoluble polymer, presumably formed by cleavage of the ring to form a derivative of glutaconaldehyde which then polymerized. A similar polymer was formed when the salts were dissolved in liquid ammonia. With thiosulfate ion, a good nucleophile, the reaction was quite slow. However, 22.9% of the theoretical amount was consumed in 3 days at room temperature.

The question of resonance interaction between the ring and the vinyl group is somewhat ambiguous, however. Doering and Schreiber[12] have investigated the addition of thiosulfate ion to vinyltrimethylammonium salts and found that only 5% reaction occurred under conditions similar to those used here. Vinyldimethylsulfonium salts, however, consumed thiosulfate ion rapidly and Doering attributes the difference to resonance stabilization of the intermediate carbanion.

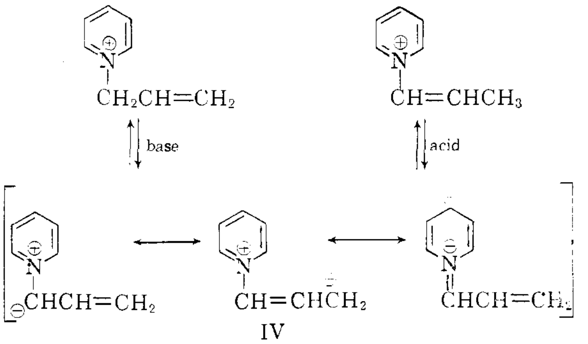


$$B^- + CH_2{=}CH\underset{CH_3}{\overset{+}{S}}CH_3 \longrightarrow \left[BCH_2\overset{-}{C}H\underset{CH_3}{\overset{+}{S}}CH_3 \longleftrightarrow BCH_2CH{=}\underset{CH_3}{S}CH_3 \right]$$

This necessitates the use of the 3d-orbitals of sulfur which are not available in the case of the vinyltrimethylammonium salts. Since classical resonance forms such as III can be written for the addition of base to the N-vinylpyridinium ion it would appear, by inference, that such resonance is not important since the rate of addition of thiosulfate ion was not significantly greater than in the case of vinyltrimethylammonium salts.

The ultraviolet spectra seemingly support this conclusion. As shown in Table IV, the N-vinylpyridinium salts absorb more strongly than simple alkylpyridinium salts but there is no shift in the absorption maximum as would be expected from observation of the spectra of other vinyl and phenyl substituted compounds.

Over against this negative evidence, however, is the observation of tritium exchange in N-allylpyridinium perchlorate. It was found that four hydrogen atoms exchanged under the mild conditions used, as shown in Table V. This could arise only if there were a facile exchange between allyl and propenyl forms, involving the resonance indicated for the ylid intermediate IV.



IV

If irreversible rearrangement from allyl to propenyl were all that occurred, then only one (or two) hydrogens would exchange. This was observed in the rearrangement of allyl to propenyl sulfides by Tarbell and Lovett[13] who also found that propenyl sulfides *do not* exchange. In addition, Doering and Hoffman[14] have found that tetramethylammonium iodide exchanges only 1.13% with deuterium in 358 hours at 100° with 0.292 *M* deuteroxide ion as catalyst. This indicates that mere proximity to a positive nitrogen does not labilize the hydrogens. The evidence, therefore, clearly indicates the presence of some additional resonance interaction and this most probably involves the pyridinium ring as shown above.

Polymerization of N-vinylpyridinium perchlorate or fluoborate was readily accomplished by means of ionizing radiation or ordinary free radical initiators, such as azobis-(isobutyronitrile). Cationic polymerization could not be initiated by boron trifluoride etherate in glacial acetic acid at room temperature. In liquid ammonia, a brick-red, toluene-soluble polymer very different from the poly-(vinylpyridinium perchlorate) was obtained. The polymerizations with ionizing radiation were carried out by exposing both crystalline salts and solutions

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[11] A. F. Roche and R. M. Price, Paper presented at Cleveland, Ohio, Spring Meeting of the American Chemical Society, 1951.

[12] W. von E. Doering and K. C. Schreiber, *J. Am. Chem. Soc.*, **77**, 514 (1955).

[13] D. S. Tarbell and W. E. Lovett, *ibid.*, **78**, 2261 (1956).

[14] W. von E. Doering and A. K. Hoffman, *ibid.*, **77**, 521 (1955).

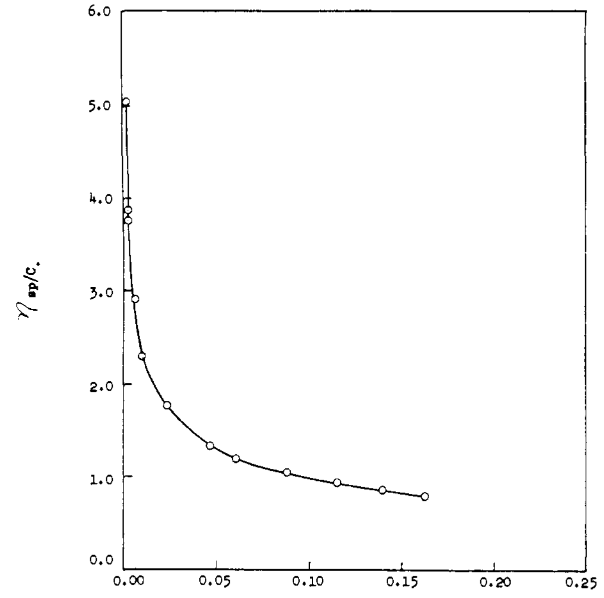

Fig. 1.—Viscosity of N-vinylpyridinium fluoroborate polymerized by γ radiation: solvent, water; temp., 30.00 ± 0.01°.

to a Co^{60} source yielding about 500,000 rep./hour. The irradiated crystals, except for yellowing, were unchanged in external appearance. X-Ray diffraction patterns, however, revealed none of the original crystallinity remaining, but showed instead two sharp bands and two broad bands which would indicate that polymerization had occurred in preferred crystallographic directions (see Table I). This would leave the polymer chains in an ordered array such as might account for the two new sharp reflections. Further substantiation for this is found in the fact that dissolution of the "crystals" and reprecipitation yielded a completely amorphous polymer whose X-ray pattern showed only two diffuse amorphous reflections. The polymers formed by free radical polymerization and by irradiation in both solid state and solution had identical infrared spectra and analyzed properly for the monomer involved.

TABLE I

X-RAY DIFFRACTION PATTERNS N-VINYLPYRIDINIUM FLUOROBORATE MONOMER AND POLYMER

Compound	Lattice spacings, Å.	Relative intensity
N-Vinylpyridinium fluoroborate	8.34	0.1
	7.02	.15
	6.42	.25
	6.10	.15
	5.66	.15
	5.30	.1
	4.79	.5
	4.62	.1
	4.48	.5
	4.14	1.0
	3.69	0.5
N-Vinylpyridinium fluoroborate crystals	3.83	1.0
irradiated with γ-radiation	3.46	0.3
	11.47[a]	
	4.29[a]	
N-Vinylpyridinium fluoroborate, polymer	10.39[a]	
	4.19[a]	

[a] Amorphous bands.

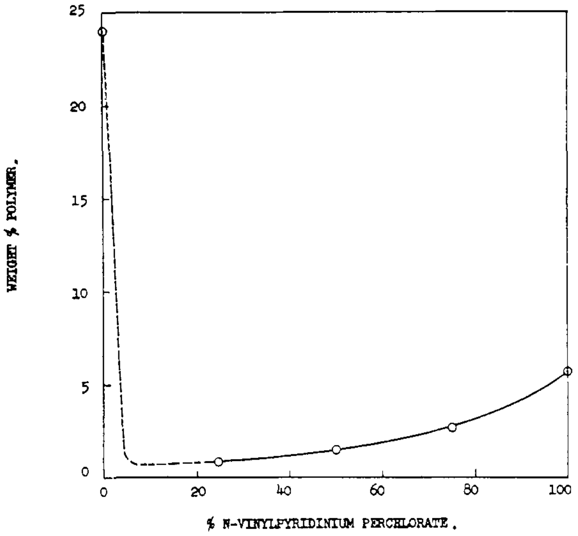

Fig. 2.—Copolymerization of styrene with N-vinylpyridinium perchlorate: catalyst, 0.7 mole % 2,2′-azobis-(isobutyronitrile).

These polymers are, of course, polyelectrolytes and exhibit the anomalous viscosity behavior of such materials, *i.e.*, the reduced viscosity η_{sp}/C rapidly increases as zero concentration is approached. Figure 1 shows this relation for N-vinylpyridinium fluoborate polymerized in the crystalline state with α-radiation. Fuoss[15] has shown that these data can be rectified by plotting in the form

$$\frac{A}{(\eta_{sp}/C) - D} = 1 + B\sqrt{C} \qquad (1)$$

where A and D are characteristic of the polymer, B is characteristic of the solvent and ηsp and C are the specific viscosity and concentration, respectively. For the data in Fig. 1, A is found to be 9.1, and since for a similar polymer, poly-(4-vinylpyridinium bromide), A is reported[16] to be directly proportional to the square of the molecular weight, the molecular weight for this polymer can be estimated at about 156,000.

The vinyl group in the N-vinylpyridinium salts would be expected to be electron deficient due to the adjacent positive charge and as such it was expected to copolymerize rapidly with electron rich monomers (negative *e*-monomers in the Alfrey–Price scheme) such as styrene ($e = -0.8$) or vinyl acetate ($e = -0.4$). The reverse was found to be true, however. The salts copolymerized poorly or not at all with negative *e* monomers, but fairly readily with positive ones, such as methyl methacrylate or acrylonitrile. Figure 2 demonstrates the retardation of polymerization in the N-vinylpyridinium perchlorate–styrene system. No polymer at all was obtained when α-methylstyrene or vinyl acetate were the comonomers. Copolymerizations with positive *e* comonomers are reported

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(15) R. M. Fuoss and G. I. Cathers, *Polymer Sci.*, **4**, 97 (1949).

(16) R. M. Fuoss, *Disc. Faraday Soc.*, **11**, 125 (1951).

TABLE II

REACTIVITY RATIOS OF N-VINYLPYRIDINIUM FLUOROBORATE

Monomer 1	Monomer 2	r_1	r_2	r_1r_2
N-Vinylpyridinium fluoroborate	Methyl methacrylate	0.008	4.75	0.038
	Methyl acrylate	.2	1.5	.23
N-Vinylpyridinium fluoroborate	Acrylonitrile	.20	1.06	.21

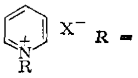
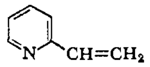
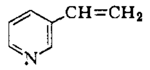
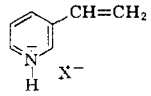
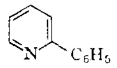
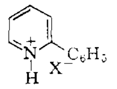
TABLE III

Q- AND e-VALUES FOR N-VINYLPYRIDINIUM FLUOROBORATE

Comonomer	e	Q Calcd. from r_1	Q Calcd. from r_2
Methyl methacrylate	2.2	0.31	0.32
Methyl acrylate	1.7	0.74	0.52
Acrylonitrile	2.4	1.88	1.86

TABLE IV

ULTRAVIOLET SPECTRA OF PYRIDINE DERIVATIVES

 X⁻ R =	Solvent	Max.	ε	Max.	ε	Ref.
CH_2CH_2Br	Water			258	4,580	This work
$CH{=}CH_2$	Water			258	8,380	This work
H	Water			257	5,100	18
C_6H_5	Methanol			282	8,500	22
	Ethanol	235	12,600	277.5	5,010	19
	95% ethanol	238	11,380	278	2,760	20
	95% ethanol	246	7,910	287	3,350	20
	Water	240	13,000	277	10,000	21
	Water	242	8,000	295	14,000	21

in Table II. The reactivity ratios as determined under the conditions described herein demonstrate that the pyridinium salt is considerably less reactive than any of the comonomers used.

The Q- and e-values calculated from these reactivity ratios are shown in Table III. As suspected, the vinyl group has a large positive e-value, indicating an extremely electron-poor double bond. Indeed, the only monomer for which a more positive e has been reported is vinylidene cyanide, $e = +2.8$. The agreement between the e-values is satisfactory. However, the values for Q do not check and it appears that the Alfrey–Price equation does not fit this system exactly. The fact that sizable Q-values were obtained, however, indicates the presence of resonance stabilization of the radical derived from the N-vinylpyridinium monomer.

The lack of agreement among the values for Q from different determinations seems to indicate that the Alfrey–Price equation may not fit accurately the case where one (or both) of the monomers is an ion. One of the basic assumptions of the Q, e scheme[17] is that the distance between radical and monomer in the propagation transition state is the same for the four possible pairs, M^*_1–M_1, M^*_1–M_2, M^*_2–M_2, M^*_2–M_1. The wide applicability of the Q–e method indicates the validity of the assumption for dipolar species. However, it may not be true where poles are involved. If the Q–e equations are rewritten so as to avoid this assumption, they become

$$r_1 = \frac{Q_1}{Q_2} \exp - \left(\frac{C_1C_1}{R_{11}DkT} - \frac{C_1C_2}{R_{12}DkT}\right) \tag{2}$$

$$r_2 = \frac{Q_2}{Q_1} \exp - \left(\frac{C_2C_2}{R_{22}DkT} - \frac{C_2C_1}{R_{21}DkT}\right) \tag{3}$$

since

$$k_{12} = P_1Q_2 \exp - \frac{C_1C_2}{R_{12}DkT} \text{ and } r_1 = \frac{k_{11}}{k_{12}}$$

Equation 3, which reduces to the familiar equation

$$r_2 = (Q_2/Q_1) \exp - [e_2(e_2 - e_1)] \tag{4}$$

if $R_{11} = R_{12} = R_{22} = R_{21}$, and $e \cong C/\sqrt{RDkT}$, can be rearranged into the form

$$2.303 \log Q_1 = \left(2.303 \log \frac{Q_2}{r_2} - e_2^2\right) + e_2 \left(\frac{C_1\sqrt{R_{22}DkT}}{R_{12}DkT}\right) \tag{5}$$

Equation 5 is a linear equation of the form $y = A + Bx$ where A and B can be calculated from experimental or known data.

In the copolymerization of two positive e monomers, one of which bears a positive ionic charge, the repulsion between species should lead to a decrease in R in the transition state since the radical and monomer would have to approach one another more closely before bond forming would overcome repulsion. If monomer 1 is the ionic species, then $R_{22} > R_{21} \cong R_{12} > R_{11}$, and further R_{12} and R_{21} should be smaller the more positive e_2 is. Since from equa-

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(17) T. Alfrey and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947).

(18) J. A. Moede and C. Curran, *J. Am. Chem. Soc.*, **71**, 857 (1949).

(19) R. P. Mariella, L. F. A. Peterson and R. C. Ferris, *ibid.*, **70**, 1494 (1948).

(20) M. L. Swain, A. Eisner, C. F. Woodward and B. A. Brice, *ibid.*, **71**, 1343 (1949).

(21) M. E. Straumanis and G. F. Doctor, *ibid.*, **73**, 3492 (1951).

(22) D. Craig, L. Schaefgen and W. P. Tyler, *ibid.*, **70**, 1624 (1948).

TABLE V

EXCHANGE OF N-ALLYLPYRIDINIUM FLUOROBORATE AT 25° WITH $H_2{}^3O$ IN PRESENCE OF PYRROLIDINE

Salt concn., *M*	Base concn., *M*	Time, days	No. H's exchanged
0.046	None	7	0.0
0.068	0.031	6	4.1, 3.9

TABLE VI

VARIATION OF Q_1 WITH e_2 OF THE COMONOMER

Comonomer	Calcd. Q_1 for N-vinylpyridinium fluoroborate	e_2 of comonomer
Methyl methacrylate	0.31	0.4
Methyl acrylate	0.61	0.6
Acrylonitrile	1.9	1.2

tion 5 log Q_1 is seen to vary inversely with R_{12}, it follows that log Q_1 and e_2 will increase simultaneously, although not in direct proportion.

This conclusion is qualitatively supported by the data in Table VI. The indication is, therefore, that the simple assumption of constant R is not sufficiently accurate in this case.

It is interesting to note that the equation used by Barb and Ham[23,24] involving the penultimate group, that is

$$n - 1 = \frac{r_2'x(r_2x + 1)}{r_2'x + 1}$$

where n is the ratio of monomer 2 to monomer 1 in the copolymer, x is the ratio of monomer 2 to monomer 1 in the reaction mixture, $r_2 = k_{222}/k_{221}$ and $r_2' = k_{122}/k_{121}$, fits the experimental data less exactly than the standard copolymerization equation.

[23] W. G. Barb, *J. Polymer Sci.*, **11**, 117 (1953).

[24] G. E. Ham, *ibid.*, **55**, 169 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, EMORY UNIVERSITY, ATLANTA 22, GA.]

Complete Analysis of the Proton Magnetic Resonance Spectrum of Furan by Means of C^{13}-H Patterns

BY G. S. REDDY AND J. H. GOLDSTEIN

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The n.m.r. spectrum of furan has been studied in acetone solution under conditions of very high resolution. The spectrum consists of two quartets, instead of the two triplets originally observed. Accurate and unambiguous values for all four coupling constants were obtained from the C^{13}-H spectrum, observed in natural abundance. With these results it was then possible to carry out an analysis of the entire spectrum of normal furan, leading to a calculated spectrum in good agreement with the observed spectrum. The values of the adjacent and cross-ring coupling constants obtained, 1.75 c.p.s. and 0.85 c.p.s., establish quite clearly that the early assumptions of the equality of these two coupling constants is not justified.

Introduction

The proton magnetic resonance spectra of furan, thiophene and pyrrole have been the subjects of a number of investigations in recent years,[1-7] in part directed toward the clarification of erroneous inferences originally derived from the simple spectral patterns of these heterocyclic compounds. According to early studies, the spectrum of thiophene consists of two closely-spaced triplets from which it was concluded that the *ortho* (adjacent) and *para* (cross-ring) coupling constants were equal. On this basis thiophene was considered as an A_2B_2 system. Subsequent investigations of thiophene in polar solvents, such as acetone and dimethyl sulfoxide, provided more complex patterns which were analyzed as AA'BB' systems with the result that the adjacent and cross-ring coupling constants were demonstrated to be unequal.

Furan has been studied in a variety of solvents. Its spectrum is strictly first-order, consisting of two rather widely separated triplets, which were originally interpreted on the basis of an assumed equality of adjacent and cross-ring coupling constants. Subsequently, Abraham and Bernstein[5] and Gutowsky, *et al.*,[8] called attention to another possible interpretation of these spectra. From the theoretical expressions for the allowed transitions in AA'BB' systems, which contain the coupling constants only as sums and differences, it can be shown that the observed triplet spacing of 1.3 c.p.s. in furan is actually half the sum of the adjacent ($J_{\text{adj.}}$) and cross-ring constants (J_{cross}). It is only on the assumption of an A_2B_2 system that the observed first-order triplet spacings provide the value of $J_{\text{adj.}} = J_{\text{cross}}$. If the system is actually AA'BB' it is impossible to determine separately the values of $J_{\text{adj.}}$ and J_{cross}, as well as the values of J_{AA} and J_{BB}, from the observed spectrum.

As a means of eliminating this indeterminacy, Abraham and Bernstein[5,6] adopted for furan the mean values of the appropriate coupling constants determined in a series of substituted furans, having shown that these values were roughly constant over the series. By this procedure they were able to obtain satisfactory agreement between the calculated and observed spectra of furan. However, since both hypotheses, *i.e.*, $J_{\text{adj.}} = J_{\text{cross}}$ and $J_{\text{adj.}} \neq J_{\text{cross}}$, led to satisfactory agreement with experiment, there was still no clear-cut basis for a choice between the two alternative interpretations. Moreover, it has been well established that n.m.r. coupling constants are more or less sensitive to substitu-

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[1] R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **37**, 1056 (1959).

[2] H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, *J. Am. Chem. Soc.*, **79**, 4596 (1957).

[3] E. J. Corey, G. Slomp, S. Dev, S. Tobinaga and E. R. Glazier, *ibid.*, **80**, 1204 (1958).

[4] J. B. Leane and R. E. Richards, *Trans. Faraday Soc.*, **55**, 518 (1955).

[5] R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

[6] R. J. Abraham and H. J. Bernstein, *ibid.*, **39**, 905 (1961).

[7] S. Gronowitz and R. A. Hoffman, *Arkiv. kemi.*, **13**, 279 (1958).

[8] D. M. Grant and H. S. Gutowsky, *J. Chem. Phys.*, **34**, 699 (1961).