Pyrolysis of α,α-Di-(β-dimethylaminoethyl)-α-phenylacetonitrile Monohydrochloride.—The monohydrochloride (29.6 g.) was placed in a 300-cc. flask, to which an air condenser was attached, and heated in a metal-bath which was maintained at 270–290°. As soon as the salt melted, trimethylamine was evolved. After about 6 minutes the salt had melted completely, and after ten minutes the evolution of gas had practically stopped. The cold, light brown, glass residue (the material becomes crystalline if rubbed under ether) was dissolved in a warm mixture of 20 cc. of water and 5 cc. of hydrochloric acid. The aqueous, acidic solutions, obtained from three experiments, were combined and the solution was made strongly alkaline. The precipitated nitrile was extracted with ether, the extract dried over magnesium sulfate, the solvent removed and the residue fractionated. The Demerol nitrile boiled at 119–122° (1–2 mm.); yield 47.1 g. (78.5%). The distillate solidified completely; m.p. 53°.[8] The hydrochloride melted at 222–224°[9] after recrystallization from absolute ethanol; mixed m.p. with an authentic sample 222–224°. The picrate melted at 247°[10] after recrystallization from methanol.

The evolved trimethylamine was passed into methyl bromide dissolved in chloroform, and the precipitated tetramethylammonium bromide (77%)[11] was analyzed.

Anal. Calcd. for $C_4H_{12}NBr$: Br, 51.87. Found: Br, 51.84.

Pyrolysis of a Mixture of Molecular Equivalent Amounts of the Base and the Dihydrochloride; Pyrolysis of the Dihydrochloride.—A mixture of 12.9 g. (0.05 mole) of the base and 16.5 g. (0.05 mole) of the dihydrochloride was heated in a bath at 260–280° (bath temperature) for 10 minutes and then at 280–310° for another 10 minutes. After the reaction mixture had been treated in the described manner, 14.2 g. (71%) of pure Demerol nitrile was obtained; m.p. 53°.

The dihydrochloride (22.5 g.) was heated in the manner described above. There was obtained 7.5 g. (55%) of Demerol nitrile. The hydrochloride melted at 222–224°.

(8) O. Eisleb (*Ber.*, **74**, 1433 (1941)), m.p. 53°.

(9) Reference 8, m.p. 221–222°.

(10) F. Bergel, A. L. Morrison and H. Rinderknecht (*J. Chem. Soc.*, 265 (1944)), m.p. 249–250°.

(11) A small amount of trimethylamine escaped from the solution.

COLLEGE OF PHARMACY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN   RECEIVED DECEMBER 14, 1951

Wien Effect in Polyelectrolytes

BY FREDERICK E. BAILEY, ANDREW PATTERSON, JR., AND RAYMOND M. FUOSS

If polyvinylpyridine is quarternized by the addition of butyl bromide, a typical polyelectrolyte is obtained. The statistical coil characteristic of the neutral polymer is distended by the intramolecular repulsion among the built-in cations; this is, however, partially screened by the counter ions which are held in the volume of the coil by the total cationic field. The equilibrium between free and associated counter ions is, of course, a dynamic one. (Here, we define free counter ions as those in the solvent between the polyions, and associated counter ions as those within the average radius of the polymer coil.) The associated counter ions do not contribute to anion current[1] and the conductance of a polyelectrolyte is therefore less than that of the corresponding monomeric salt at the same concentration. The polycation naturally has no sharp boundary, on account of intramolecular Brownian motion; we may, however, imagine a zone in which

(1) W. R. Huizenga, P. E. Grieger and F. T. Wall, THIS JOURNAL, **72**, 2636 (1950).

the potential energy of a cation is of the order of kT and define this zone as the periphery of the polycation. Inside this region, a counter ion will be considered as associated with the polycation. A small decrease in potential energy should therefore suffice to remove some of the peripheral counter ions, and thereby increase the population of free ions, and with it the conductance. We would then expect[2] a fairly large Wien effect[3] for polyelectrolytes. The purpose of this note is to present preliminary results which confirm this prediction and which presumably may be taken as additional evidence confirming our model.

A sample of poly-4-vinyl-N-n-butylpyridinium bromide[4] was used which has a degree of polymerization of approximately 2000. Strauss[4] found a reduced viscosity of about 12 at a concentration of 0.001 monomolar; the equivalent Einstein sphere would have a radius of the order of 500 Å. Conductances were measured by the Differential Pulse Transformer bridge method[5] over the range 9–18 kv./cm., at 25.00° at a concentration of 0.00105 monomolar in water. Pulse widths of 4, 6 and 11 μsec. were used; balancing was performed visually on single pulses. The experimental results are summarized in Fig. 1, where relative increase in specific conductance, $\Delta\kappa/\kappa_0$, is plotted against field strength in kv./cm. Here, κ_0 is conductance at low voltages and for all practical pur-
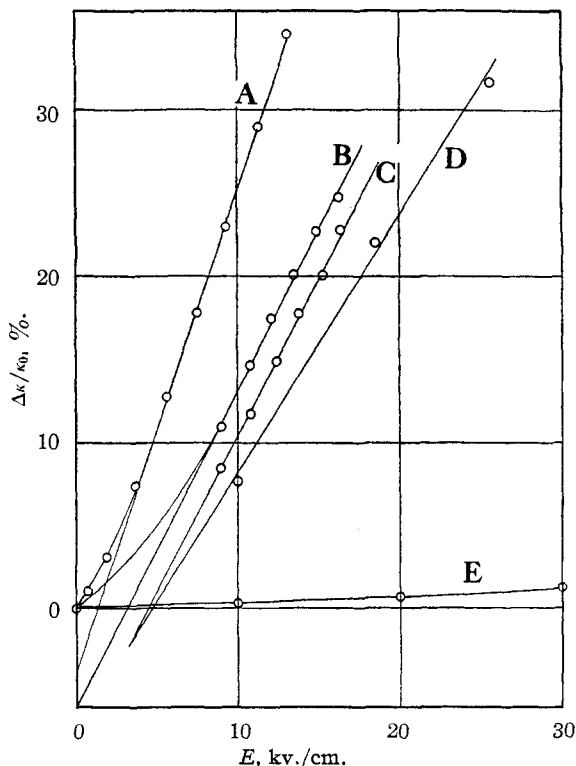

Fig. 1.—Wien effect of poly-4-vinyl-N-n-butylpyridinium bromide: A, $(Bz)_3NHPi$; B, 11 μsec.; C, 6 μsec.; D, 4 μsec.; E, $MgSO_4$.

(2) D. Edelson and R. M. Fuoss, *ibid.*, **72**, 306 (1950).

(3) H. C. Ekstrom and C. C. Schmelzer, *Chem. Revs.*, **24**, 367 (1939).

(4) R. M. Fuoss and U. P. Strauss, *Trans. N. Y. Acad. Sci.*, **51**, 836 (1949).

(5) J. A. Gledhill and A. Patterson, Jr., *Rev. Sci. Instruments*, **20**, 960 (1949).

poses equals the limiting conductance at zero field strength. It will be seen that a marked Wien effect is present; at only 10 kv./cm., the conductance is increased by 13%. For comparison, the lower curve is for 0.0001 molar magnesium sulfate[6] in water; this is a salt which is considered to have a fairly large Wien effect. By way of further contrast, the upper curve is for tribenzylammonium picrate[7] in toluene at 35°. We see that the polyelectrolyte in water gives about as large a Wien effect as does a 1-1 salt in a solvent whose dielectric constant is only 2.35. If we interpret our result as a second Wien effect in terms of Onsager's theory,[8] the polyelectrolyte is behaving approximately like a salt in which the cation has a charge of +33 (the ratio of the dielectric constants of water and toluene); in other words, the presence of about 1.7% of the counter ions in the peripheral zone mentioned above would be sufficient to account for our result.

The balance patterns (Fig. 2) observed on the oscilloscope for different pulse lengths are significant, if we consider the distances a bromide ion can travel during a pulse. At 10 kv./cm., a counter ion trav-

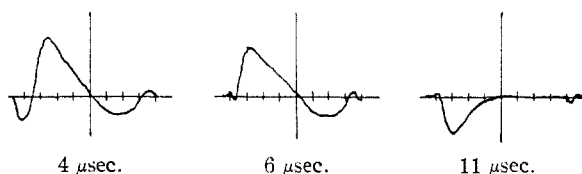4 μsec.   6 μsec.   11 μsec.

Fig. 2.—Balance patterns.

els about 3000 Å. in 4 μsec. The balance patterns are tracings taken from the oscilloscope; a horizontal line coinciding with the center graticule marking is an indication of impedance balance. On the 11 μsec. tracing, balance was achieved after a preliminary excursion (i.e., unbalance) lasting almost 5 μsec. On the shorter pulses balance was apparently not reached during the period of the pulse. Measurements taken with pulse lengths shorter than that necessary to give a steady state conductance value are accordingly only approximate estimates of the conductance. This behavior is, however, a clear indication of a time of relaxation effect in which the relaxation time is of the order of 1-5 microseconds. In such a time any free counter ions could travel several thousand Å. under the influence of a field of 10 kv./cm.

In addition to this relaxation time phenomenon, it was noticed that the low field conductance of the solution was not regained instantaneously, as is usually the case with ordinary electrolytes. Figure 3 shows approximately the behavior observed. The low field conductance was regained slowly after the increase due to the high field, and then a decrease was observed, followed by a return to the normal low field conductance after a few minutes. This behavior was reproducible. On the other hand, two high field measurements made one immediately after the other were quite reproducible. The same phenomenon could be obtained with the applica-

(6) M. Wien, Ann. Physik, 85, 795 (1928); F. E. Bailey, unpublished results.

(7) R. M. Fuoss, D. Edelson and B. I. Spinrad, This Journal, 72, 327 (1950).

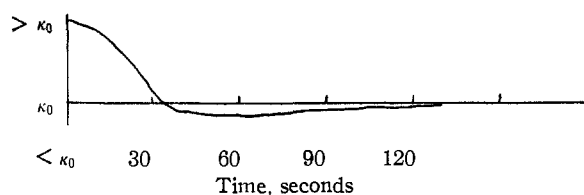(8) L. Onsager, J. Chem. Phys., 2, 599 (1934).

Fig. 3.—Time dependence of balance.

tion of a d.c. potential of 3 volts applied to the cell for a few seconds. In all cases the power dissipated in the cell was sufficient to raise the temperature of the electrolyte no more than 0.002°. The phenomenon of Fig. 3 is presumed to require more explanation than to ascribe it to electrode effects.

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN 11, CONNECTICUT

Preparation and Properties of Some Unsaturated Sulfonium Salts[1]

BY GEORGE B. BUTLER AND BEN M. BENJAMIN

Ray and Levine[2] found that in the reaction between organic sulfides and alkyl halides, the sulfonium salt first formed can decompose in a variety of ways, the tendency being toward formation of the salt having the organic radicals of lowest molecular weight. The possibility exists that each alkyl radical may exist at some time as the alkyl halide. The final result is formation of the most stable product. These workers obtained trimethylsulfonium bromide by treating dimethyl sulfide with phenyl-2-fluorenylbromoethane and by treating phenyl-2-fluorenylmethylmethyl sulfide with methyl iodide, obtained trimethylsulfonium iodide.

In attempting to prepare unsaturated sulfonium halides, we have observed that when an alcohol is used as solvent, the alkyl radical of the alcohol may enter the sulfonium salt. Methanol[3] has been recommended as a suitable solvent for sulfonium salt formation. In attempting to prepare sulfonium halides of diallyl sulfide in methanol solution, only trimethylsulfonium halides were obtained. Methyl iodide, isopropyl iodide, phenacyl bromide and p-phenylphenacyl bromide were used as reactants. Diallyl-p-phenylphenacylsulfonium bromide has been reported[2]; however, in our attempts to prepare this compound, only trimethylsulfonium bromide was obtained. Dimethylallyl sulfide in methanol solution when treated with allyl iodide resulted in formation of trimethylsulfonium iodide. One previous unsuccessful attempt[4] to prepare triallylsulfonium salts has been reported, although allyldipropylsulfonium iodide was obtained. It has been stated[5] that dialkenyl sulfides, e.g., diallyl sulfide, part with their sulfur when treated with excess of methyl iodide. In addition to diallyl-p-phenylphenacylsulfonium bromide[2] and allyldipropylsul-

(1) This work was done under the sponsorship of the Office of Naval Research under Contract No. N7 onr-346.

(2) F. E. Ray and I. Levine, J. Org. Chem., 2, 267 (1937).

(3) R. W. Bost and H. C. Schultz, This Journal, 64, 1165 (1942).

(4) W. Steinkopf and R. Bessaritsch, J. prakt. Chem., 109, 230 (1925).

(5) P. D. Ritchie, "Chemistry of Plastics and High Polymers," Cleaver–Hume Press, Ltd., London, p. 186.