[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Alkali Metal Polymerization. Further Proof of an Ion-Radical Intermediate[1]

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The reaction of methyl vinyl sulfone with the blue solution of potassium in bis-2-ethoxyethyl ether was investigated. Polymerization did not occur, but the dimer, 1,4-bis(methyl sulfonyl)butane (IV) was obtained. This suggests strongly an ion-radical mechanism for at least part of the reaction with potassium catalysis. IV was also obtained with lithium in tetrahydrofuran and in hexane. The implications of the structure of the dimer are discussed.

Recently, O'Driscoll and Tobolsky,[3] and Overberger, Pearce, and Mayes[4] have independently proposed that lithium catalysis of vinyl polymerization proceeded by a one-electron transfer from lithium metal to monomer to form an ion-radical. The ion-radical initiated propagation step proceeded through either an anionic path accompanied by dimerization of the radicals[4-7] or by a combination of radical and anionic propagation steps.[3] The catalytic action of sodium and potassium has been observed to be different from lithium, the results from the former indicating a more anionic mechanism from homopolymerization[8-11] and copolymerization[3b,12] experiments.

The ion-radical as an intermediate in the lithium catalyzed reaction was implicit in the experimental observations,[3,4] but no direct proof was available. The data[3,8-12] on sodium or potassium catalyzed polymerizations did not imply such an intermediate, but at the same time did not exclude the possibility. In the course of an investigation of alkali metal catalyzed polymerizations, the formation of the ion-radical as an intermediate in both potassium- and lithium-catalyzed reactions has been verified. Quite recently, C. E. Frank and coworkers[13,14] have reported high yields of the dimerized ion-radical product from carefully controlled reactions of sodium dispersion with styrene, α-methylstyrene, and butadiene.

The polymerization of methyl vinyl sulfone with alkali metals was investigated in our laboratories. Lithium in liquid ammonia could not be used in this study since it was found that ammonia readily adds to methyl vinyl sulfone, even at Dry Ice temperatures. The blue solution formed by dissolving potassium in bis-2-ethoxyethyl ether[15,16] was investigated as a catalyst for the polymerization reaction. The blue solution of potassium was prepared at −78° and maintained at that temperature to minimize decomposition. It had been noted that on warming, a grayish blue deposit forms and in time the solution becomes colorless. High vacuum techniques were necessary to insure purity and prevent contamination from air and moisture. Meticulously cleaned and dried glassware required heating at 110–120° under high vacuum (10^{-6} mm.) overnight to ensure stability and formation of the blue solution. When methyl vinyl sulfone was added, with stirring, to the blue solution, the color slowly changed to a yellow amber. Termination with methanolic hydrochloric acid caused a lightening of the color to a pale yellow. Polymer was not obtained in any experiment, even with a twenty-four-hour reaction time. After evaporation of solvent and treatment with methanol, a solid was obtained. The yield approximated the reaction of one mole of potassium with somewhat less than one mole of methyl vinyl sulfone. On recrystallization from water, a white solid was obtained and the infrared spectrum exhibited a medium peak at 722 cm.$^{-1}$, indicative of a tetramethylene grouping.[17]

The compound was deduced to be 1,4-bis(methyl sulfonyl)butane (IV) presumably arising *via* the following reaction sequence:

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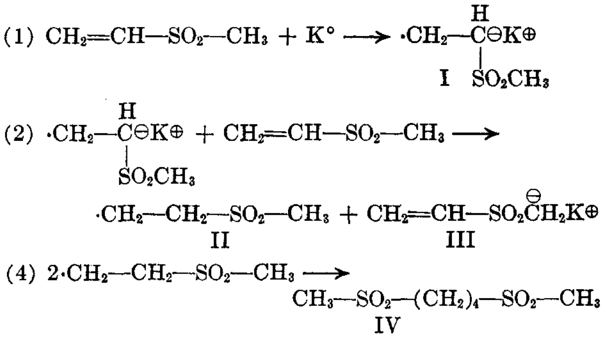

$$(1)\ CH_2{=}CH{-}SO_2{-}CH_3 + K^{\circ} \longrightarrow \cdot CH_2{-}\overset{H}{\underset{SO_2CH_3}{C}}{}^{\ominus}K^{\oplus}\quad \text{I}$$

$$(2)\ \cdot CH_2{-}\overset{H}{\underset{SO_2CH_3}{C}}{}^{\ominus}K^{\oplus} + CH_2{=}CH{-}SO_2{-}CH_3 \longrightarrow$$

$$\underset{\text{II}}{\cdot CH_2{-}CH_2{-}SO_2{-}CH_3} + \underset{\text{III}}{CH_2{=}CH{-}SO_2\overset{\ominus}{C}H_2K^{\oplus}}$$

$$(4)\ 2\cdot CH_2{-}CH_2{-}SO_2{-}CH_3 \longrightarrow \underset{\text{IV}}{CH_3{-}SO_2{-}(CH_2)_4{-}SO_2{-}CH_3}$$

It is felt that the anion radical I formed by transfer of an electron to methyl vinyl sulfone underwent a fast reaction with the acidic methyl group of another monomer molecule yielding the radical II and the anion III, the anion III being too weak a base to initiate polymerization. The radicals then could dimerize, yielding the product IV. It is considered unlikely that dimerization occurred at −78° prior to the acid-base reaction due to the high activation energy necessary for the formation of a 1,4-dianion. The possibility that dimerization of the ion-radical occurs before exchange cannot be completely rejected at this point, but the suggested mechanism is supported by the work of Szwarc and Levy[7b] wherein it was found that the dimerization of ion-radical was a slow step.

To prove the structure of the compound, 1,4-bis(methyl sulfonyl)butane (IV) was synthesized by the hydrogen peroxide oxidation of 1,4-bis-(methylthio)butane prepared from 1,4-butanedithiol and dimethyl sulfate.

The infrared spectrum of the compound from the methyl vinyl sulfone–potassium-bis-2-ethoxyethyl ether reaction was identical in all respects to that of 1,4-bis(methyl sulfonyl)butane and a mixed melting point was not depressed.

1,4-Bis(methyl sulfonyl)butane was also obtained when methyl vinyl sulfone reacted with lithium dispersion in tetrahydrofuran and in hexane. The yields were quite low, presumably due to the heterogeneous nature of the reaction.

The formation of 1,4-bis(methyl sulfonyl)butane suggests strongly that alkali metal-catalyzed polymerizations involve an ion-radical intermediate, and that this mechanism is operative for the experiments with potassium and lithium. The work of Frank and co-workers[13,14] adds to the above evidence for the ion-radical intermediate. The fact that IV was the only isomer found with methyl vinyl sulfone is of interest. Overberger, Baldwin, and Gregor[18] studied the copolymerization of butyl vinylsulfonate, an analogous monomer. It was found that the butyl vinylsulfonate radical was not appreciably resonance stabilized. Price and Zomlefer[19] studied the copolymerization of methyl vinyl sulfone. Their data indicated a lack of resonance stabilization of a free radical by the sulfone group. The formation of IV as the preferred isomer substantiates the lack of radical stabilization by a sulfone group and stabilization of the negative charge at the alpha carbon atom.

After this investigation had been carried out, Dainton and co-workers[20,21] reported on polymerizations initiated by blue solutions of potassium in dimethoxyethane. They were able to polymerize styrene reproducibly, but acrylonitrile gave erratic results and methyl methacrylate did not polymerize at all. In the course of our work, it was found that both methacrylonitrile and methyl isopropenyl ketone gave erratic results with potassium in bis-2-ethoxyethyl ether. Methyl vinyl sulfide did not polymerize.

EXPERIMENTAL[22]

Reagents for polymerizations. Methyl vinyl sulfone was prepared by the method of Buckley, Charlish, and Rose.[23] The infrared spectrum duplicated the reported spectrum,[24] n_D^{20} 1.4635 (n_D^{20} 1,4640, 1.4636).[24] The monomer was purified for each run by passage through alumina followed by degassing, distillation on a vacuum line and storage at −190° until needed.

Bis-2-ethoxyethyl ether (Ansul Ether 141, Ansul Co.) was purified by one of two methods: (a) refluxing with lithium aluminum hydride for several hours followed by distillation at reduced pressure—the middle fraction boiling at 76°/32 mm. was collected and stored over calcium hydride under helium; (b) passage through a column of Woelm alumina, basic, activity 1, and storage over calcium hydride under helium.

Tetrahydrofuran and hexane were purified as described in ref. 25.

Other monomers were purified in a manner similar to methyl vinyl sulfone. Helium and argon were passed through a column of Linde Molecular Sieves and Drierite.

Reaction of methyl vinyl sulfone with potassium in bis-2-ethoxyethyl ether. All experiments were carried out on a high vacuum line to ensure freedom from air and moisture. The method of preparation of the blue solution of potassium in bis-2-ethoxyethyl ether was adopted from Cafassa and Sundheim.[16] The glassware was cleaned in an acid bath, thoroughly rinsed with deionized water and oven dried (a bisulfite rinse was also used in one experiment but did not alter the results). The reactor[4,11] was assembled on the vacuum line and baked at 110–120° for 18 hr. while pumping at 10^{-6} mm. Connections were through standard tapered 24/40 joints lightly greased with Dow Corning high vacuum silicone grease. In a typical experiment, 100 ml. of bis-2-ethoxyethyl ether was treated with sodium-potassium alloy at −78° for 18 hr. after degassing. Potassium, 10^{-3} mole, was charged under a flow of helium to the reactor. The

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potassium pellet was pressed out under hexane from freshly cut potassium metal in a calibrated metal die.[11] The reactor was pumped at 10^{-6} mm. for 60 min. Methyl vinyl sulfone, 3 ml., distilled and dried over calcium hydride, was distilled to a tube connected to the reactor and frozen at −190°. A potassium mirror was formed on the reactor wall and the bis-2-ethoxyethyl ether distilled onto the mirror using a Dry Ice–acetone bath as a condensing agent. A blue solution formed during distillation. After the bis-2-ethoxyethyl ether distillation was complete, the sealed-in magnetic stirrer was started, the monomer thawed and added to the blue solution by tipping the tube. Reaction temperature was maintained by a Dry Ice–acetone bath. The color changed to a yellow amber within less than 30 sec. The reaction was terminated by introducing helium into the reactor and the addition of 10 ml. of 1*N* methanolic hydrochloric acid. The color then changed to a pale yellow and the solvent was stripped off under vacuum. The residual oil was added to methanol and after filtering and drying, 99 mg. of a brownish solid was obtained, crude m.p. 185–198°. This represented a 93% yield based on an equimolar reaction with charged potassium. The solid was taken up in hot water, treated with decolorizing charcoal, and the solution allowed to slowly evaporate until crystallization occurred, 60 mg. (74%), m.p. 202–203.5°; a mixed melting point with authentic IV, 202–203.5°.

Preparation of 1,4-bis(methyl sulfonyl)butane (IV). 1,4-Butanedithiol, 50 g. (0.41 mole) was dissolved in a solution of 40 g. (1 mole) of sodium hydroxide in 200 ml. of water. Dimethyl sulfate, 78 ml. (0.82 mole) was added dropwise with stirring and slight cooling over a 60-min. period. The reaction was stirred overnight, the oil was taken up in chloroform and the combined extracts dried over anhydrous magnesium sulfate. The chloroform was removed under vacuum and the residue fractionated. 1,4-Bis(methylthio)butane, 48.3 g., 78%, was collected at 135–137°/48 mm., n_D^{27} 1.5103, d_4^{25} 0.8322.

Anal. Calcd. for $C_6H_{14}S_2$: C, 48.00; H, 9.35; S, 42.67. Found: C, 48.69; H, 9.56; S, 42.65.

Hydrogen peroxide, 30%, 79.1 g., (0.7 mole) was added dropwise with stirring during a 60-min. period to 23 g. (0.15 mole) of 1,4-bis(methylthio)butane containing 0.5 ml. of phosphoric acid. The temperature was allowed to rise slowly of its own during the addition. The reaction was refluxed for 2.5 hr. and the reaction mass solidified on cooling. The solid was recrystallized twice from water, 19.8 g. (60%), m.p. 202.5–203.5°.

Anal. Calcd. for $C_6H_{14}O_4S_2$: C, 33.64; H, 6.54; O, 29.91; S, 29.91. Found: C, 33.90; H, 6.86; O, 29.87; S, 30.21.

Methyl vinyl sulfone-lithium-hexane. Methyl vinyl sulfone, 0.7 g., and 20 ml. of hexane were charged to the reactor and thoroughly degassed on the vacuum line. Lithium dispersion, 75 mg. of a 30% dispersion, was added under argon. The reaction was stirred at room temperature for 16 hr. under argon. After termination, the mixture was evaporated to near dryness. A small amount of crystals were left behind—these were stirred with methanol, filtered and dried. After recrystallization from water, 10 mg. of 1,4-bis(methylsulfonyl)butane was obtained, m.p. 200–202°; a mixed melting point with authentic IV, melted at 201–203°.

Methyl vinyl sulfone-lithium-tetrahydrofuran. Methyl vinyl sulfone, 2.1 ml., and 50 ml. of tetrahydrofuran were charged and degassed throughly on the vacuum line. Lithium dispersion, 177 mg. of a 30% dispersion was added under argon and the reaction was stirred overnight under argon. After termination the reaction was treated as above. Only a few milligrams of product was obtained; a mixed melting point with authentic IV, melted at 198–201°.

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BROOKLYN, N.Y.

[CONTRIBUTION FROM THE LABORATORY OF PHARMACEUTICAL CHEMISTRY,
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Ethylene and Phenylacetyl Chloride in the Friedel-Crafts Reaction. Novel Syntheses of 2-Tetralones and Benzofuranones[1]

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Phenylacetyl chloride and *p*-methoxyphenylacetyl chloride were treated separately with ethylene and aluminum chloride to give, respectively, 2-tetralone and 6-methoxy-2-tetralone. Under the same conditions, 2,3-dimethoxyphenylacetyl chloride failed to react with ethylene but instead underwent monodemethylation and ring closure to the benzofuranone.

Together with other investigators,[4–6] we have been interested in employing appropriately substituted 2-tetralones as intermediates for the preparation of morphine and morphine-like compounds. While 1-tetralones are readily obtained through cyclization of substituted phenylbutyric acids, 2-tetralones are much more difficult to synthesize. Heretofore, preparation of 2-tetralones has been hampered either by poor yields or difficulty accessible raw materials or both. Numerous examples are

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