JOURNAL OF POLYMER SCIENCE VOL. XXXVI, PAGES 329-332 (1959)

Copolymerization Characteristics of Pentachlorophenyl Vinyl Sulfide

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Price and Morita[1] have reported on the copolymerization of phenyl vinyl sulfide and have suggested that steric hindrance prevents the coplanarity thought to be necessary for conjugation through the sulfur atom. In contrast to this, there is conjugation through the sulfur atom of divinyl sulfide.[2]

The present investigation extends the comparison to pentachlorophenyl vinyl sulfide in which the *ortho* chlorine atoms unquestionably prevent coplanarity. It also shows the effect of the powerfully electron withdrawing pentachlorophenyl ring[3] upon the monomer reactivity constants Q and e.

EXPERIMENTAL*

Pentachlorophenyl vinyl sufide was prepared[3a] by vinylation of pentachlorothiophenol. Pentachlorothiophenol was dissolved in aqueous alkali metal carbonate or acid phosphate and heated at 190°C. with acetylene at a total pressure of 200 psig. The product distilled at 110°C./0.05 mm. It could be recrystallized from benzene-methanol and sublimed under vacuum at 60–70°C. The pure vinyl sulfide melted at 74.6–75.3°C. Carbon analyses of this compound and its derivatives were consistently low.

Anal. Calcd. for $C_8H_3Cl_5S$: C, 31.14; H, 0.98; Cl, 57.48; S, 10.40. Found: C, 27.83; H, 0.94; Cl, 57.58; S, 10.32.

The mass spectrum showed a large parent peak at mass 306 containing five chlorine atoms and a second large peak at mass 236 containing three chlorine atoms, one sulfur atom, and not more than eight carbon atoms. The infrared spectrum run in Fluorolube and Nujol mulls is summarized in Table I. It shows the C=C stretching at 6.32 μ and the out-of-plane deformations of the vinyl hydrogen atoms at 10.55 and 11.40 μ.

Pentachlorophenyl Vinyl Sulfoxide. The vinyl sulfide was oxidized with hydrogen peroxide in acetic acid-acetic anhydride-benzene at 0°C. to

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* Melting points are uncorrected; elemental analyses are by Dow Special Services Laboratory.

TABLE I
Infrared Spectrum of Pentachlorophenyl Vinyl Sulfide (2.5–15 μ)

λ, μ	Intensity	λ, μ	Intensity
6.32	Medium	9.07	Medium
6.71	Weak	9.27	Weak
7.25	Weak	9.91	Medium
7.48	Very strong	10.55	Strong
7.57	Very strong	11.40	Strong
7.62	Very strong	12.36	Very weak
7.88	Medium	13.93	Very weak
8.28	Weak	14.51	Strong
8.56	Weak	14.95	Medium

form the vinyl sulfoxide in 20% yield. The sulfoxide was recrystallized from benzene-alcohol, alcohol, and hexane, then sublimed to give white needles melting at 131–134°C. In the infrared spectrum of the sulfoxide, the C═C stretch is much weaker than in the vinyl sulfide. The hydrogen out-of-plane deformation bands are present and a band at 9.2 μ is possibly due to S—O stretch.

Anal. Calcd. for $C_8H_3Cl_5SO$: C, 29.61; H, 0.93; S, 9.88. Found: C, 25.36; H, 1.23; S, 9.93.

ar-Tetrachloro-ar-(Vinylthio)benzenethiol. To a solution of 200 g. (0.65 mole) of vinyl sulfide in 400 ml. pyridine was added a solution of 42 g. (0.73 mole) sodium hydrogen sulfide in 200 ml. of water plus 200 ml. of diethylene glycol. The mixture was refluxed overnight, cooled, and poured into 3 l. of water. A small precipitate was removed and discarded. The filtrate was acidified by the addition of concd. hydrochloric acid. The precipitate which formed was washed with water and dried. It melted at 81–85°C. and weighed 125 g. (63% yield). After recrystallization from aqueous acetone and sublimation, the melting point was 84.2–86.2°C. Infrared analysis showed S—H, S—CH═CH_2, and hexasubstituted benzene.

Copolymerization. The styrene used was freshly distilled and free of inhibitors. The methyl acrylate was redistilled before use. Commercial grades of solvents were used.

In the copolymerization runs, 3 to 7 g. of monomer mixture containing 0.1% of azobisisobutyronitrile was sealed under vacuum at −70°C. in a Pyrex bomb. The bomb was placed in a bath at 80°C. for a period of five minutes to two hours, then chilled and opened. The copolymers were dissolved in benzene and precipitated in methanol. After reprecipitation, they were dried overnight in a vacuum oven at 90°C.

Tables II and III list the experimental data. For those runs in which the conversion exceeded 10%, the value of M_2 was corrected for conversion.[4] The styrene copolymers softened in a capillary tube at 140 to 165°C. Styrene copolymers containing over 20 mole-% vinyl sulfide would not continue to burn when the powder, on a spatula, was withdrawn from a gas flame. A compression molding of a styrene copolymer with $[\eta] = 0.58$ and $m_2 = 0.12$ had a Vicat softening point of 122°C.

TABLE II

Styrene (M_1)-Pentachlorophenyl Vinyl Sulfide (M_2) Copolymers

Run	M_2	Time, hr.	% conv.	% Cl	% S	m_2(Cl)	m_2(S)
1	0.16	0.75	5	8.75	1.34	0.057	0.047
2	0.32	1.50	6	14.55	2.51	0.103	0.097
3	0.50	0.75	5	25.75	4.30	0.215	0.193
4	0.67	2.00	9	34.11	6.15	0.330	0.329
5	0.80	0.75	7	40.88	7.37	0.453	0.451
6	0.91	0.75	12	50.20	8.80	0.700	0.650

TABLE III

Methyl Acrylate (M_1)-Pentachlorophenyl Vinyl Sulfide (M_2) Copolymers

Run	M_2	Time, min.	% conv.	% Cl	% S	m_2(Cl)	m_2(S)
1	0.10	7	23	14.58	3.17	0.087	0.108
2	0.20	5	26	25.04	5.30	0.178	0.225
3	0.30	13	28	35.15	5.96	0.279	0.272
4	0.46	10	12	37.84	7.31	0.350	0.398
5	0.66	15	10	43.91	7.90	0.475	0.469
6	0.89	10	2.6	50.27	9.63	0.662	0.803

DISCUSSION

The relative reactivity ratios,[5] r_1 and r_2, listed in Table IV are weighted averages calculated by the method of Joshi and Kapur.[6] The monomer constants,[7] Q and e, for pentachlorophenyl vinyl sulfide were evaluated by plotting the reactivity ratios on a Q-e map, using published values[7b] of Q and e for styrene and methyl acrylate. The values obtained are $Q = 0.23 \pm 0.04$ and $e = -0.62 \pm 0.20$.

Thus the reasonance (Q) factor for pentachlorophenyl vinyl sulfide is smaller than for either phenyl vinyl sulfide[1] ($Q = 0.32$) or methyl vinyl sulfide[8] ($Q = 0.35$). The electrical (e) factor for pentachlorophenyl vinyl sulfide is less negative than for either phenyl vinyl sulfide[1] ($e = -1.3$) or methyl vinyl sulfide[8] ($e = -1.5$). These results are consistent with somewhat lowered resonance stabilization of the radical derived from pentachlorophenyl vinyl sulfide and the donation by the sulfur atom of less

TABLE IV

Relative Reactivity Ratios

M_1	M_2	r_1	σr_1	r_2	σr_2
Styrene	Vinyl sulfide	3.9	0.2	0.24	0.08
Methyl acrylate	Vinyl sulfide	0.89	0.26	0.25	0.30

electronic charge to the vinyl group when a good electron sink is attached to the sulfur atom.

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Synopsis

Pentachlorophenyl vinyl sulfide was prepared by vinylation of pentachlorothiophenol in aqueous buffers. The preparation of pentachlorophenyl vinyl sulfoxide and of *ar*-tetrachloro-*ar*-(vinylthio)benzenethiol are described. The copolymerization of pentachlorophenyl vinyl sulfide with styrene and with methyl acrylate was studied. The monomer reactivity constants of pentachlorophenyl vinyl sulfide ($Q = 0.23$, $e = -0.6$) indicate less resonance stabilization of the radical and less electron density in the vinyl group than is the case with phenyl vinyl sulfide or methyl vinyl sulfide.

Résumé

Le sulfure de vinyle-pentachlorophényle a été préparé par vinylation du pentachlorothiophénol en solutions tampons. Les préparations du sulfoxyde de vinyle-pentachlorophényle et du aryltétrachloro-aryl(vinylthio)-benzène-thiol ont été décrites. La copolymérisation du sulfure de vinyle-pentachlorophényle avec le styrène et l'acrylate de méthyle a été étudiée. Les constantes de réactivité du sulfure de vinyle-pentachlorophényle ($Q = 0{,}23$; $e = -0{,}6$) laissent apparaitre moins de stabilisation par résonance du radical et une plus faible densité électronique dans le groupement vinylique que dans le cas du sulfure de vinylephényle ou du sulfure de vinyle-méthyle.

Zusammenfassung

Pentachlorphenylvinylsulfid wurde durch Vinylierung von Pentachlorthiophenol in gepufferter, wässriger Lösung dargestellt. Die Darstellung von Pentachlorphenylsulfoxyd und von Tetrachlor-(vinylthio)-thiophenol wird beschrieben. Die Copolymerisation von Pentachlorophenylvinylsulfid mit Styrol und Methylmethacrylat wurde untersucht. Die Monomer-reaktionsfähigkeitskonstanten von Pentachlorvinylsulfid ($Q = 0{,}23$, $e = -0{,}6$) lassen eine geringere Resonanzstabilisierung des Radikals und eine geringere Elektronendichte in der Vinylgruppe erkennen, als es beim Phenylvinylsulfid oder Methylvinylsulfid der Fall ist.

Received May 29, 1958