water. The chelate then was dried over phosphorus pentoxide at 0.1 mm. for 16 hours.

Anal. Calcd. for $C_{14}H_{10}O_2N_2Co$: C, 56.58; H, 3.39; N, 9.43. Found: C, 56.55; H, 3.65; N, 9.28. Calcd. for $C_{14}H_{10}O_2N_2Ni$: C, 56.63; H, 3.39; N, 9.44. Found: C, 56.55; H, 3.42; N, 9.41, 9.56. Calcd. for $C_{14}H_{10}O_2N_2Cd$: C, 47.95; H, 2.87; N, 7.99. Found: C, 49.32; H, 3.22; N, 8.64, 8.75.

When the chelates were prepared from tetrahydrofuran solutions of the azine, similar analytical values were obtained and in addition a copper chelate was formed which apparently contained one mole of water of hydration.

Anal. Calcd. for $C_{14}H_{10}O_2N_2Cu \cdot H_2O$: C, 52.57; H, 3.80; N, 8.76. Found: C, 51.98; H, 3.60; N, 8.50.

Polyazine of 5,5′-Methylene-bis-salicylaldehyde. a. Acetic Acid Solution.—5,5′-Methylene-bis-salicylaldehyde (6.4063 g., 0.025 mole) was dissolved in 300 ml. of acetic acid. The solution was heated on a steam-bath to 90–95° and a solution of hydrazine sulfate (3.2533 g., 0.025 mole) in 100 ml. of water was added in one portion. The reaction was stirred at 90–95° for six hours, cooled and filtered to give 7.0 g. of product (76%). It was redissolved in dimethylacetamide and precipitated in 5% aqueous sodium chloride solution. The polymer was collected, washed thoroughly and dried. The infrared spectrum is compatible with the proposed polyazine structure: broad band ~3500 cm.$^{-1}$, chelated hydroxyl; intense band 1630 cm.$^{-1}$, >C=N— stretching; 1325 cm.$^{-1}$, phenolic -OH. The infrared spectrum resembles that of salicylaldehyde azine quite closely with the exception of a strong band at 1655 cm.$^{-1}$ indicating aromatic aldehyde end groups.

Anal. Calcd. for $(C_{15}H_{12}O_2N_2)x$: C, 71.41; H, 4.79; N, 11.11. Found: C, 69.31; H, 4.85; N, 8.61.

b. **Pyridine Solution.**—To a solution of 4.1000 g. (0.016 mole) of 5,5′-methylene-bis-salicylaldehyde dissolved in 600 ml. of pyridine (temperature 80°, nitrogen atmosphere) was added 20 ml. of glacial acetic acid and 1 ml. (0.016 mole) of hydrazine hydrate (85% solution). The solution was brought to reflux and within 30 minutes a gelatinous yellow precipitate separated. After four hours reflux, pyridine was distilled off to a final volume of 100 ml. The resultant suspension was poured into a dilute solution of acetic acid and the polymer which precipitated was collected, washed and dried; yield 4.1 g., quantitative, inherent viscosity 0.118 (0.2% in sulfuric acid).

Anal. Calcd. for $(C_{15}H_{12}O_2N_2)n$: C, 71.41; H, 4.79; N, 11.11. Found: C, 69.23; H, 5.31; N, 8.51.

The analysis corresponds to a low molecular weight polymer with a D.P. of 4 to 6 and with aldehyde end groups.

Dimeric Azine of 5,5′-Methylene-bis-salicylaldehyde.—In a 500-ml. flask was placed a solution of 8.1616 g. (0.03185 mole) of 5,5′-methylene-bis-salicylaldehyde in 400 ml. of pyridine; 10 ml. of acetic acid was added, followed by 20 ml. of 85% hydrazine hydrate (0.3185 mole) (10× excess). The solution was refluxed for five hours and the product isolated by pouring the reaction mixture into two liters of dilute acetic acid. It was washed with dilute acetic acid, water, and dried to give 9.2 g. (90%) of a yellow powder which analyzed for the dimeric azine with hydrazone end groups.

Anal. Calcd. for $C_{30}H_{28}O_4N_6$: C, 68.51; H, 5.11; N, 14.24. Found: C, 68.52; H, 5.22; N, 14.65.

Polyazine of Bis-salicylaldehyde-5,5′-sulfone.—In a one-liter flask was placed a solution of 4.9006 g. (0.016 mole) of bis-salicylaldehyde-5,5′-sulfone and 20 ml. of acetic acid in 300 ml. of pyridine. At a temperature of 80°, 1 ml. (0.016 mole) of hydrazine hydrate was added and the solution brought to reflux. Within three minutes the solution had become cloudy yellow. After five hours reflux, pyridine was distilled off to a final volume of 100 ml. and then poured into dilute acetic acid. The polymer was isolated by filtration, washed and dried; yield 3.7 g. (76%).

Anal. Calcd. for $(C_{14}H_{10}O_4SN_2)n$: C, 55.62; H, 3.33; N, 9.27; S, 10.61. Found: C, 55.62; H, 3.81; N, 8.79; S, 10.75.

Thermal Stabilities.—The thermal stabilities of the metal chelates of salicylaldehyde azine and the polyazines of 5,5′-methylene-bis-salicylaldehyde and of bis-salicylaldehyde-5,5′-sulfone were determined by a thermobalance similar to that described by Winslow and Matreyek.[8] The results are given in Tables III and IV.

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[8] F. H. Winslow and W. Matreyek, *J. Polymer Sci.*, **22**, 315 (1956).

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, UNIVERSITY OF NOTRE DAME AND UNIVERSITY OF PENNSYLVANIA]

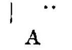
Copolymerization Characteristics of Two Vinylsilanes

BY CHARLES E. SCOTT AND CHARLES C. PRICE

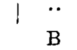
RECEIVED DECEMBER 18, 1958

Copolymerization of vinyltriethoxysilane (I) with styrene and acrylonitrile indicates the polar and resonance reactivity factors to be $e = 0.1$ and $Q = 0.03$. For vinyltrimethylsilane (II), $e = -0.1$ and $Q = 0.03$. The very low resonance factors are supported by the ultraviolet spectra of I and II, which show considerably less conjugation than methyl vinyl sulfide. The unshared 3p-electrons on the latter thus would seem to be more important for resonance than vacant 3d orbitals on both sulfur and silicon.

In earlier studies of copolymerization and spectra of vinyl sulfides[1] and related compounds, it seemed evident from the relatively large resonance stabilization factor in copolymerization,[2] $Q = 0.3$–0.4, and the relatively intense ultraviolet absorption band, λ_{max} 225–240, E_{max} *ca.* 10,000, for vinyl sulfides, that a sulfide sulfur atom can provide appreciable resonance stabilization for an adjacent odd electron, either in the free-radical intermediate in copolymerization or in the excited state.


$-\overset{\cdot}{\underset{|}{C}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}-R$

A


$-\underset{|}{C}=\underset{\cdot\cdot}{\overset{\cdot}{S}}-R$

B

For the corresponding sulfones, the resonance factor in copolymerization is markedly reduced, $Q \simeq 0.07$, as is the ultraviolet absorption, λ_{max} *ca.* 210, E_{max} *ca.* 300.[1,3]

The purpose of the present investigation of vinylsilanes was to determine to what extent the difference between sulfide and sulfone was due to lack of unshared 3p electrons on the latter sulfur rather than its marked difference in electrical charge. The silicon atom of a vinylsilane would not have the strong electron-attracting inductive effect of the sulfone group but would have similar available 3d orbitals.

Experimental[4]

Styrene was redistilled under reduced pressure in a stream of nitrogen, b.p. 38° (13 mm.). Acrylonitrile was

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[1] C. C. Price and J. Zomlefer, THIS JOURNAL, **72**, 14 (1950); C. C. Price and R. D. Gilbert, *ibid.*, **74**, 2073 (1952); C. C. Price and H. Morita, *ibid.*, **75**, 4747 (1953).

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

[3] E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 231 (1949).

[4] Microanalyses by Micro-Tech Laboratories, Skokie, Ill.

redistilled at atmospheric pressure under nitrogen, b.p. 76.0°. **Dimethylformamide** was redistilled under reduced pressure, b.p. 47° (13 mm.), $n^{20}D$ 1.4320. All were stored under nitrogen at 5° until used.

Vinyltriethoxysilane.—Vinyltrichlorosilane[5] (80 g., b.p. 89–91°, 0.5 mole) was added over two hours to 300 ml. of stirred, ice-cold absolute ethanol, protected from atmospheric moisture. After standing overnight at room temperature, excess ethanol and hydrogen chloride were removed *in vacuo* at 60–70°. Distillation of the residue under nitrogen through a 12-inch helix-packed column gave 63 g. (66%), b.p. 78–80° (41 mm.), $n^{25}D$ 1.3970 (lit.[6] b.p. 63° (20 mm.), $n^{25}D$ 1.3960).

Vinyltrimethylsilane was prepared from the trichloride and methylmagnesium bromide according to Nagel and Post,[7] b.p. 54.5–55°, $n^{25}D$ 1.3888, yield 39% (lit.[7] b.p. 55°, $n^{20}D$ 1.3902).

Copolymerization Procedure.—Copolymerization of pairs of monomers was carried out in sealed nitrogen-flushed Pyrex test-tubes containing a total of 0.08 mole of the monomers and 0.00016 mole of azobisisobutyronitrile held at 60 ± 0.1°. In each case polymerization was interrupted when it was estimated that about 5% of copolymer had formed. The copolymers were precipitated by pouring the reaction mixture into 200 ml. of cold methanol. The precipitated polymer was collected by filtration, washed with alcohol and air-dried. The samples were further purified by dissolving them in the least amount of filtered solvent. After reprecipitation by dropwise addition to cold methanol, the polymers were recovered by filtration and dried overnight at 30° and 1 mm.

The results of copolymerizations of vinyltriethoxysilane with styrene and with acrylonitrile in DMF are summarized in Tables I and II. Similar copolymerizations with vinyltrimethylsilane are summarized in Tables III and IV.

TABLE I

COPOLYMERIZATION OF STYRENE (M_1) WITH VINYLTRIETHOXYSILANE (M_2)[a]

M_2	Time, hours	Conversion, %	Softening point, °C.[b]	C, %	H, %	O and Si,[c] %	m_2
0.200	5	7	160–187	91.32	7.85	0.83	0.012
.297[d]	3	2	151–170	90.67	8.00	1.33	.021
.429[e]	7.5	5	124–155	90.25	7.85	1.90	.027
.500[e]	1	1	130–157	88.74	7.93	2.33	.048
.598[e]	7.5	3	138–157	88.76	8.04	3.20	.048
.878[f]	15	1	110–140	83.82	8.19	7.99	.122

[a] Catalyst, azo-bis-isobutyronitrile. [b] Capillary tube method. [c] Calculated by difference. [d] Benzene (3 ml.) added as solvent. [e] Minute amounts of copolymer had precipitated from monomer mixtures. [f] Benzene (4 ml.) added as solvent.

TABLE II

COPOLYMERIZATION OF ACRYLONITRILE (M_1) WITH VINYLTRIETHOXYSILANE (M_2)[a]

M_2[b]	Time, hours	Conversion, %	C, %	H, %	N, %	N, %[c]	m_2
0.200	3	3	63.97	6.25	22.85	23.08	0.038
.301	3	3	60.73	6.61	20.30	20.50	.074
.401	6	6	61.56	6.84	18.07	18.25	.111
.494	17	4	60.53	7.10	15.71	15.87	.156
.600	43	d					
.801	48	d					

[a] Catalyst, azo-bis-isobutyronitrile. [b] In 4 ml. of DMF as solvent. [c] Corrected nitrogen values.[8] [d] No detectable conversion.

TABLE III

COPOLYMERIZATION OF STYRENE (M_1) WITH VINYLTRIMETHYLSILANE (M_2)[a]

M_2[b]	Time, hours	Conversion, %	C, %	H, %	m_2
0.203	4	1	91.72	7.94	0.018
.435[c]	4	2	91.32	7.93	.032
.599[c]	5	2	90.19	7.88	.070
.790	4	2	90.11	8.39	.073

[a] Catalyst, azo-bis-isobutyronitrile. [b] Benzene (3 ml.) added as solvent. [c] Polymer solution became slightly turbid prior to quenching.

TABLE IV

COPOLYMERIZATION OF ACRYLONITRILE (M_1) WITH VINYLTRIMETHYLSILANE (M_2)[a]

M_2[b]	Time, hours	Conversion, %	C, %	H, %	N, %	N, %[c]	m_2
0.207	2.0	3	66.25	6.58	22.56	22.79	0.079
.400	21	4	65.41	4.72	20.30	20.50	.134
.494	23	5	64.63	7.24	18.74	18.92	.176
.604	24	1	64.50	7.80	16.44	16.66	.242

[a] Catalyst, benzoyl peroxide. [b] In 4 ml. of DMF as solvent. [c] Corrected nitrogen values.[8]

Ultraviolet absorption spectra were determined in isooctane solution using a Beckman DU spectrophotometer with Process and Instruments automatic recorder. Vinyltriethoxysilane (1.51×10^{-3} mole/l.) showed λ_{max} 210, E_{max} 300 and **vinyltrimethylsilane** (1.3×10^{-4} mole/l.). λ_{max} 202, E_{max} 1470.

Discussion

The copolymerization characteristics of vinyltriethoxylsilane and vinyltrimethylsilane are summarized in Table V.

TABLE V

COPOLYMERIZATION CHARACTERISTICS OF VINYLTRIETHOXYSILANE AND VINYLTRIMETHYLSILANE (M_2)

M_2	M_1	r_1	r_2	Q_2	e_2
$(OEt)_3$	Styrene[a]	22 ± 5	0	0.03[c]	0.10[c]
	Acrylonitrile[b]	5 ± 1	0		
$(CH_3)_3$	Styrene	26 ± 8	0	0.031[c]	−0.14[c]
	Acrylonitrile	3.9 ± 3	0.07 ± 0.03	0.035	−0.10

[a] $Q = 1.0$, $e = -0.8$. [b] $Q_2 = 0.44$, $e = 1.2$. [c] By solving $r_1 = (Q_1/Q_2) \exp(-e_1(e_1 - e_2))$ and $r'_1 = (Q'_1/Q_2) \exp(-e'_1(e'_1 - e_2))$.

The low values of Q for both monomers (0.03–0.035) are further supported by recent data reported by Pike and Bailey[9a] and Thompson.[9b] For copolymerization of vinyltriethoxysilane (M_2) with acrylonitrile (M_1) and with vinyl chloride (M'_1), Thompson reports values of $r_1 = 0.9$ and $r'_1 = 4.5$. From these data, and using $Q'_1 = 0.024$ and $e'_1 = 0.2$ for vinyl chloride, we find $Q_2 = 0.02$ and $e_2 = 0.2$. These very low values for Q, compared to $Q = 0.015$ for ethyl vinyl ether[10] and $Q = 0.35$ for methyl vinyl sulfide,[1a] indicate that silanes resemble the ether far more closely than the sulfide. If the resonance stabilization in the latter case involves a $2p$–$3p$ π-bond, this is not available in the ether or the silane and would account for the facts observed.

The lesser tendency for resonance stabilization with silicon receives further support from the ultraviolet spectra data. Both triethoxy- and trimeth-

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(5) We are grateful to Linde Air Products Co. for a generous supply of this chemical.

(6) R. Nagel, C. Tamborski and H. Post, *J. Org. Chem.*, **16**, 1768 (1951).

(7) R. Nagel and H. Post, *ibid.*, **17**, 1379 (1952).

(8) C. C. Price and C. E. Greene, *J. Polymer Sci.*, **6**, 111 (1952).

(9) (a) R. M. Pike and D. L. Bailey, *J. Polymer Sci.*, **22**, 55 (1956); (b) B. R. Thompson, *ibid.*, **19**, 373 (1956).

(10) C. C. Price and T. C. Schwan, *ibid.*, **16**, 577 (1955).

ylvinylsilanes absorb at lower wave length and much lower intensity than vinyl sulfides.

These facts suggest that it is misleading to refer to the radical-sulfide resonance interaction as "*d*-orbital" resonance. A 3*d* orbital must be utilized in the process but it appears likely that it must be used to hold the unshared 9th electron on the sulfur atom (B). If the double bond in (B) were indeed a 2*p*–3*d* double bond, it could be expected that silicon could participate in such interaction equally well.

The electrical factors observed for the vinylsilanes seem to be about as expected, intermediate between sulfide ($e = -1.4$)[1] and sulfone ($e = 1.2$).[1] The more positive *e*-value for the triethoxy compound could be ascribed to the electron-withdrawing inductive effect of the oxygen atoms as compared to the methyl groups of the trimethyl compound.

NOTRE DAME, IND.
PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, UNIVERSITY OF NOTRE DAME AND UNIVERSITY OF PENNSYLVANIA]

Divinyl Sulfide: Copolymerization and Spectra

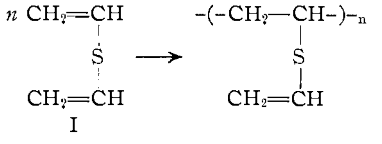
BY CHARLES E. SCOTT AND CHARLES C. PRICE

RECEIVED DECEMBER 18, 1958

Divinyl sulfide has a very intense absorption in the ultraviolet, λ_{max} 240 and 255, E_{max} 41,800 and 38,000. Earlier values are very probably those for the corresponding sulfoxide. The high degree of conjugation is reflected in the polymerization characteristics of divinyl sulfide. The material can be converted to soluble high polymer in 50% yield by azobisisobutyronitrile catalysis. Copolymerization studies indicate the resonance stabilization factor, $Q = 0.6 \pm 0.1$, to be appreciably higher than that for methyl vinyl sulfide, $Q = 0.35$.

The similarity of conjugating properties of the vinylene and sulfide groups has been emphasized by many authors.[1] The particular case of the similarity of ultraviolet spectra between divinyl sulfide and 1,3,5-hexatriene[2] has stimulated this further investigation of the conjugative properties of the former.

One example of the enhanced conjugation in divinyl sulfide (I) is the increased ease of its conversion to homopolymer, as compared to methyl vinyl sulfide. The fact that the polymer produced after 50% conversion is still soluble is itself evidence of the greater reactivity of the divinyl sulfide system than of a vinyl sulfide system. Normal vinyl polymerization of I would produce a polymer with pendant vinyl groups.



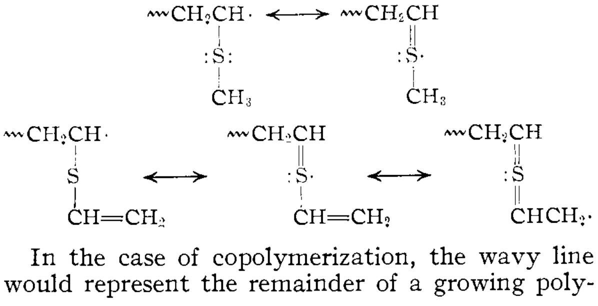
$$n\ CH_2{=}CH{-}S{-}CH{=}CH_2 \longrightarrow -(-CH_2{-}CH(S{-}CH{=}CH_2){-})_n-$$

The presence of these pendant vinyl groups is evident from the ultraviolet spectra of copolymers of I (Table IV) and from the crosslinking and insolubilization of these polymers which occurs on standing. The fact that the polymer is not highly crosslinked initially must mean that either double bond in I is far more reactive in polymerization and copolymerization than the pendant double bond in the polymer. This in turn would be most readily explained if the two vinyl groups were mutually activated by conjugation through the sulfur atom.

This through conjugation is clearly supported by the ultraviolet spectra data on I. It is pertinent to point out that we now believe that earlier reports of the spectra of I are indeed that of its sulfoxide.[3] The data in Table IV indicate the need for great care in using solvents free of peroxide impurities capable of readily oxidizing sulfide groups to sulfoxides. Thus isopropyl vinyl sulfide showed essentially the same λ_{max} and log E_{max} in alcohol and in *freshly purified* dioxane. In dioxane which had been purified earlier and stored without exclusion of air, there was an appreciable shift of the absorption to longer wave length and lower intensity, closely resembling the sulfoxide.

The ease of oxidation of the sulfide group by peroxide is also supported by the ineffectiveness of benzoyl peroxide as a catalyst. In many monomer systems, benzoyl peroxide and azoisobutyronitrile are roughly equally effective as catalysts. In divinyl sulfide polymerizations, the former is ineffective, presumably due to its rapid destruction by reaction with the sulfide group.

Copolymerization studies of I (M_1) with methyl methacrylate and styrene lend further support to the through conjugation in I. The resonance parameter, $Q_1 = 0.6 \pm 0.1$, is considerably higher than that for methyl vinyl sulfide, $Q = 0.35$. This suggests an added degree of resonance stabilization for the intermediate free radical from I.



In the case of copolymerization, the wavy line would represent the remainder of a growing poly-

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(1) See, *e.g.*, (a) A. D. Walsh, *Quart. Revs.*, **2**, 85 (1948); (b) C. C. Price and J. Zomlefer, THIS JOURNAL, **72**, 14 (1950); (c) M. R. Padhje and J. C. Patel, *Trans. Faraday Soc.*, **49**, 1119 (1953).

(2) C. C. Price and H. Morita, THIS JOURNAL, **75**, 4747 (1953).

(3) H. Mohler and J. Sorge, *Helv. Chim. Acta*, **23**, 1200 (1940), give λ_{max} 255 and 275, log E_{max} 3.7 and 3.75 (in hexane) as contrasted to our values of λ_{max} 240 and 255, log E_{max} 4.62 and 4.58 (in dioxane). The shift to longer wave length and lower intensity would correspond to that we observe for isopropyl vinyl sulfide and its sulfoxide (Table IV).