[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Monomer Reactivity Factors for Methyl Vinyl Sulfide and Sulfone. Some Comments on Covalent Sulfur Bonding

BY CHARLES C. PRICE* AND JACK ZOMLEFER[1,2]

It has been suggested that the reactivity of monomers in copolymerization, as expressed by copolymer ratios, may be interpreted in terms of two constants, Q and e, for each monomer.[3,4] The constant Q is related to the reactivity of the double bond toward a neutral free radical and is governed chiefly by the stability of the free radical in the adduct, principally influenced by possibilities for resonance stabilization through mesomeric interaction with the functional group X.

$$R\cdot + CH_2{=}CH \longrightarrow RCH_2CH\cdot$$
$$\qquad\quad X \qquad\qquad\quad X$$

The factor e involves the interaction of polar factors, perhaps principally dipoles, in the radical and the monomer as they effect the energy of the transition state.[5]

It was the purpose of the investigation reported herein to determine copolymer ratios, and thence Q and e values, for the monomers in which X = SCH_3 and X = SO_2CH_3. This seemed particularly pertinent since the data might shed further light on the problem of the nature of the sulfur–oxygen bonds in the sulfone group.[6] Recent contributions have tended to discard evidence indicating a semi-polar coördinate bond in favor of covalent double bonds involving expansion of the sulfur shell to twelve electrons.[6b,d] The nature of any conjugation of these double bonds with an adjacent unpaired electron should be reflected in the Q value of the vinyl sulfone as well as in its ultraviolet absorption spectrum. Data on the ultraviolet absorption spectra of the two olefins have therefore been included to supplement the copolymerization data.

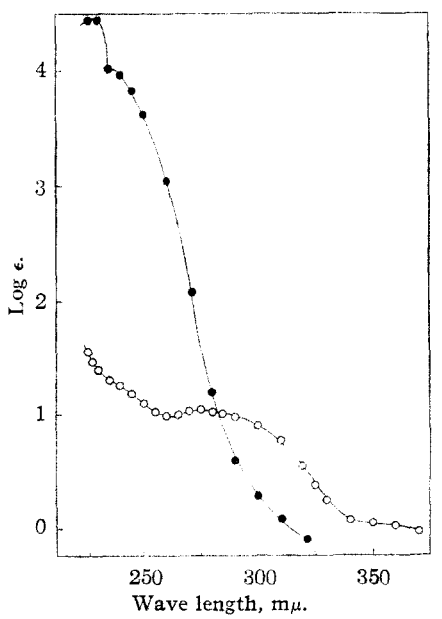

Fig. 1.—Ultraviolet absorption spectra: methyl vinyl sulfide (●) and sulfone (○).

2-Hydroxyethyl methyl sulfide was prepared according to Windus and Shildneck[7] and converted to the 2-chloroethyl sulfide according to Windus and Kirner.[8] Dehydrohalogenation to **methyl vinyl sulfide** was accomplished by sodium in amyl alcohol essentially according to Brown and Moggridge[9] in 42% yield, b. p. 66.4–66.8°, $n^{20}D$ 1.4835 (lit.,[9] b. p. 69–70°). Attempts to dehydrohalogenate by refluxing in triethylamine or quinoline led to a quantitative recovery of unreacted 2-chloroethyl methyl sulfide.

Conversion to the **vinyl sulfone** was accomplished by oxidation of the chlorosulfide with hydrogen peroxide according to Buckley, Charlish and Rose.[10] The crude chloro-sulfone was dehydrohalogenated with triethylamine to give methyl vinyl sulfone in 63% yield, b. p. 115–117° (19 mm.) (lit.,[10] b. p. 115–117° (19 mm.)).

The ultraviolet spectra were measured in 95% ethanol solution using a Beckman quartz spectrophotometer, the sulfide at concentrations ranging from 0.0145 to 0.0000145 mole/l. and the sulfone at 0.02671 mole/l. The molar extinction coefficients, $\epsilon = \log I_0/I/1 \times c$ (c in mole/l.), are summarized in Fig. 1.

Oxidation of the chloro-sulfide with just one equivalent of hydrogen peroxide, followed by treatment with methanolic alkali, gave a mixture from which two fractions were separated. One, b. p. 120–125.5° (9 mm.), $n^{20}D$ 1.4739, d^{20}_{20} 1.1183, appeared to be **2-methoxyethyl methyl sulfoxide.**

Anal. Calcd. for $C_4H_{10}O_2S$: C, 39.32; H, 8.25; S, 26.24. Found[11]: C, 38.91; H, 7.98; S, 26.41.

Another, b. p. 80–80.5° (9 mm.), $n^{20}D$ 1.4799, d^{20}_{20} 1.0827, appeared to be principally **2-hydroxyethyl methyl sulfoxide.**

Anal. Calcd. for $C_3H_8O_2S$: C, 33.30; H, 7.45; S, 29.60. Found: C, 35.60; H, 7.28; S, 27.55.

The other monomers used in the investigation were purified by distillation and center cuts taken: vinyl acetate (Niacet), b. p. 71.3–72.0°; styrene (Dow), b. p. 39.4–39.5° (9 mm.); methyl acrylate (Rohm and Haas), b. p. 80.0–80.5°.

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(2) Abstracted from a Ph.D. thesis submitted to the Graduate School of the University of Notre Dame.

(3) Alfrey and Price, *J. Polymer Sci.*, **2**, 101 (1947).

(4) Price, *ibid.*, **3**, 772 (1948); Fordyce, Ham and Chapin, THIS JOURNAL, **20**, 2489 (1948).

(5) For a more detailed analysis, see M. G. Evans, Gergely and Seaman, *J. Polymer Sci.*, **3**, 866 (1948).

(6) See, for example, (a) Sidgwick, "Some Physical Properties of the Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933; (b) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945; (c) Sutton, *J. Chem. Soc.*, 544 (1940); (d) Phillips, Hunter and Sutton, *ibid.*, 146 (1945).

(7) Windus and Shildneck, "Org. Syn.," Coll. Vol. II, p. 411 (1943).

(8) Windus and Kirner, *ibid.*, p. 136.

(9) Brown and Moggridge, *J. Chem. Soc.*, 816 (1946).

(10) Buckley, Charlish and Rose, *ibid.*, 1515 (1947).

(11) Analyses by Micro-Tech Laboratories, Skokie, Illinois.

Copolymerization of pairs of monomers was carried out in sealed nitrogen-flushed Pyrex tubes containing a total of 0.08 mole of the monomers and 0.00016 mole of benzoyl peroxide held at 60 ± 0.1°. In each case, polymerization was interrupted when it was estimated that about 5% of copolymer had formed; in some experiments, however, as much as 20% conversion had occurred. The copolymers were precipitated by pouring the reaction mixture into 200 ml. of methanol. The precipitated polymer was collected by filtration, washed with alcohol, dried and weighed to estimate per cent. conversion. Before analyses the samples were purified by reprecipitation from a solvent (chloroform, benzene or nitromethane) by pouring into cold methanol. Methyl vinyl sulfide failed to copolymerize satisfactorily with vinyl acetate but data for the other pairs are summarized in Tables I–IV. The copolymer composition calculated from sulfur and from carbon-hydrogen analysis agreed satisfactorily only for the styrene-vinyl sulfide polymer.

TABLE I

COPOLYMERIZATION OF METHYL ACRYLATE (M_1) WITH METHYL VINYL SULFIDE (M_2)

M_2[a]	Time, min.	Conversion, %	Percentages S	C	H	m_2[b] (S)	m_2[c] (C)
0.125	13	14.8	8.91	53.72	7.24	0.232	0.321
.250	13	13.5	12.81	53.23	7.46	.329	.393
.375	13	15.9	15.68	52.58	7.12	.397	.485
.500	13	14.9	17.48	52.30	7.12	.440	.525
.625	25	19.9	18.16	51.94	7.34	.457	.574
.750	55	20.0	20.57	51.63	7.32	.511	.615
.875	165	8.2	22.05	51.66	7.44	.547	.611

[a] Mole fraction of methyl vinyl sulfide in monomer mixture. [b] Mole fraction of methyl vinyl sulfide in copolymer, calculated from sulfur analysis. [c] Mole fraction of methyl vinyl sulfide in copolymer, calculated from carbon analysis.

TABLE II

COPOLYMERIZATION OF STYRENE (M_1) WITH METHYL VINYL SULFIDE (M_2)

M_2	Time, hr.	Conversion, %	Percentage S	C	H	m_2 (S)	m_2 (C)
0.125	20.25	5.95	1.00	90.71	7.96	0.032	0.048
.250	20.75	7.65	2.25	89.82	7.80	.072	.077
.375	21.25	6.55	3.12	88.81	7.72	.099	.108
.500	21.50	6.41	4.82	87.42	7.52	.150	.150
.625	22.25	4.76	6.67	85.30	7.66	.253	.257
.750	23.30	4.08	11.24	80.93	7.70	.330	.330
.875	32.00	2.31	18.44	73.37	7.80	.511	.517

TABLE III

COPOLYMERIZATION OF STYRENE (M_1) WITH METHYL VINYL SULFONE (M_2)

M_2	Time, hr.	Conversion, %	Percentages S	C	H	m_2 (S)	m_2 (C)
0.125	2.75	4.30	2.77	85.54	7.27	.0090	0.113
.250	3.50	4.14	4.54	82.03	7.43	.149	.173
.375	4.00	3.05	5.97	78.31	7.17	.195	.236
.500	5.50	3.05	7.39	74.58	6.81	.240	.300
.625	6.50	2.10	8.77	71.32	6.96	.284	.355
.750	7.50	..	..[a]				
.875	8.50	..	..				

[a] Yield too small for analysis.

TABLE IV

COPOLYMERIZATION OF VINYL ACETATE (M_1) WITH METHYL VINYL SULFONE (M_2)

M_2	Time, hr.	Conversion, %	Percentages S	C	H	m_2 (S)	m_2 (C)
0.125	2.00	15.73[a]	16.18	42.58	6.07	0.483	0.554
.250	2.17	20.43[a]	17.40	41.83	6.15	.524	.589
.375	2.50	22.33[a]	18.16	41.36	6.00	.550	.612
.500	3.67	21.38	16.96	40.70	6.01	.510	.642
.625	3.83	8.58	19.42	39.98	5.80	.594	.680
.750	4.33	4.63	21.00	38.86	5.89	.650	.736
.875	5.00	...					

[a] Precipitate formed in these mixtures shortly after polymerization began so these data were neglected in computing the copolymerization ratios.

The discrepancies in the other experiments are consistent and much greater than the experimental error in elementary analyses. An explanation of this interesting anomaly would at present be merely speculation. Since the sulfur content seems a more accurate criterion of composition, and generally much less sensitive to inclusion of foreign elements such as oxygen and fragments from the catalyst, it was considered the more reliable and was utilized for calculation of the copolymer ratios.

These ratios may be estimated by plotting r_1 against r_2 for each experiment according to the following equation[12]

$$r_2 = \frac{M_1}{M_2}\left[\frac{dM_2}{dM_1}\left(1 + \frac{M_1}{M_2}r_1\right) - 1\right]$$

The area of intersection of these lines gives some indication of the magnitude of error in r_1 and r_2. The values for r_1 and r_2 may also be estimated by a plot of monomer composition against polymer composition.[13] The experimental points, as well as the calculated curves for the chosen values for r_1 and r_2, are summarized graphically in Fig. 2.

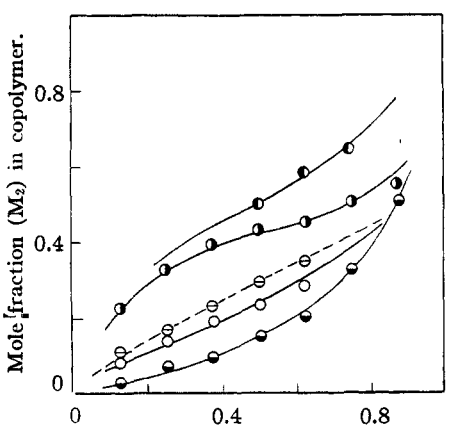


Fig. 2.—Copolymerization curves for methyl vinyl sulfide (M_2) with: styrene (M_1, ⊖) and with methyl acrylate (M_1, ◑); and for methyl vinyl sulfone (M_2) with vinyl acetate (M_1, ◐) and with styrene (M_1, O (S analysis), ⊖ (C analysis)).

(12) Lewis, Walling, Cummings, Briggs and Mayo, THIS JOURNAL, 70, 1519 (1948).

(13) Agron, Alfrey, Bohrer, Hass and Wechsler, *J. Polymer Sci.*, 3, 157 (1948).

From these values of r_1 and r_2, the values of Q and e were calculated from the equations of Alfrey and Price[3]

$$r_1 = (Q_1/Q_2)e^{-e_1(e_1-e_2)}$$
$$r_2 = (Q_2/Q_1)e^{-e_2(e_2-e_1)}$$

using the following values for Q_1 and e_1[4]: styrene, $Q = 1.0$ and $e = -0.8$; methyl acrylate, $Q = 0.42$ and $= 0.6$; vinyl acetate, $Q = 0.03$ and $e = -0.3$. The results are summarized in Table V, the estimated range of r_1 and r_2 values being indicated in parentheses.

TABLE V

COPOLYMERIZATION RATIOS AND MONOMER REACTIVITY FACTORS FOR METHYL VINYL SULFIDE AND SULFONE

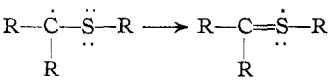
M_1	M_2	r_1	r_2	Q_2	e_2
Methyl acrylate	Sulfide	0.35 (0.3–0.37)	0.05 (0.03–0.09)	0.35	−1.4
Styrene	Sulfide	5.1 (3.5–5.5)	0.12 (0.05–0.15)	.34	−1.5
Vinyl acetate	Sulfone[a]	0.3 (0.1–0.45)	0.4 (0.35–0.5)	.07	1.2
Styrene	Sulfone	2.0 (1.3–2.4)	0.01 (0)	.11	1.2
Styrene	Sulfone (from C H data)	1.40 (1.3–1.4)	0.01 (0–0.03)	.15	1.3

[a] These values are based on copolymerization data only in the high sulfone concentration range, neglecting the low sulfone concentration range where precipitation of polymer shortly after copolymerization was initiated complicates interpretation.

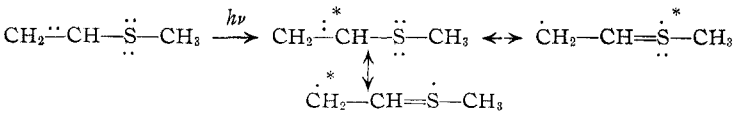
The values for the electrical factor, e, for the sulfide and sulfone are much as expected, the former being electron-donating and the latter electron-withdrawing.

The value for the free radical stabilization factor, Q, for the sulfone, which is very low, quite comparable to vinyl chloride and vinyl acetate (0.03), indicates that the sulfone group has little of the usual character of an unsaturated substituent. The lowest Q value for a substituent with a genuine covalent double bond is that for methyl acrylate (0.42). This evidence from copolymerization data, as well as the low absorption coefficient in the 220–250 mμ region, thus indicates that the sulfur–oxygen bond in a sulfone group does not have normal double bond character. These experiments thus support the view that the sulfur–oxygen bond is best described as a semipolar bond,[13a] in spite of recent interpretations to the contrary.[6b,c,d] In view of this conclusion, it seems of some interest to examine the arguments leading to the suggestion of covalent double bond character for the "oxy-bond." These seem to have centered chiefly around three types of experimental data, dipole moments, bond lengths and bond energies.[6d] It seems quite satisfactory, however, to interpret the experimental evidence in terms of a semipolar bond with a single pair of shared electrons. Because of the net positive charge on the donor atom and the net negative charge on the acceptor, it is certainly reasonable to expect this pair to be strongly polarized toward the donor atom, reducing the polarity and dipole moment of the bond. The added attraction of the net opposite charges on the donor and acceptor atoms will further result in an electrostatic force in addition to the normal covalent bond energy, accounting for shortening the bond and increasing its strength as compared to a normal non-polar covalent single bond.

The high Q value for methyl vinyl sulfide was rather surprising, indicating that a sulfide sulfur atom can provide considerable stabilization of an unpaired electron on an adjacent carbon atom. It seems that a reasonable interpretation of this stabilization would be the following mesomeric interaction.



Such an interaction would involve expansion of the sulfur octet, which is certainly permissible and possible. It is of considerable significance that, using ultraviolet absorption as a criterion, the sulfide group also shows considerable conjugative ability since the absorption for methyl vinyl sulfide shows a maximum at 240 mμ, log $\epsilon = 4.0$,[14] quite characteristic for olefin bonds conjugated with carbonyl groups. Since the primary process of photoexcitation undoubtedly involves raising one electron, presumably one of the electrons of the double bond, to an excited level, one might consider the primary excited state as a diradical in which the two "unpaired" electrons have opposite spin. The following constitutes a rough attempt to indicate this concept by formulas.



The ability of the substituent sulfide group (like any unsaturated group) to participate in mesomeric interaction in the "radical-like" excited state would, on this basis, influence the absorption process in the same way as unsaturated groups. It thus seems that the parallel influence of substituent groups on the monomer reactivity factor Q and the ultraviolet absorption can be ascribed to a certain degree of similarity between the excited state and the free radical state involved in copolymerization.

It seems pertinent to emphasize that most of

(13a) It would perhaps be more accurate to say that evidence from copolymerization data and ultraviolet spectra indicate a degree of mesomeric interaction of a carbon–carbon double bond with the sulfur–oxygen bond markedly less than that displayed with a carbonyl group. Several readers have suggested that the interaction of the sulfone group with conjugate unsaturation is similar to that of a carbonyl group in a carboxylate ion. This latter statement would seem to be equivalent to the preceding one since the carbonyl group of a carboxylate ion is far less effective in conjugative properties than a normal carbonyl group

(14) See also Fehnel and Carmack, THIS JOURNAL, 71, 2889 (1949).

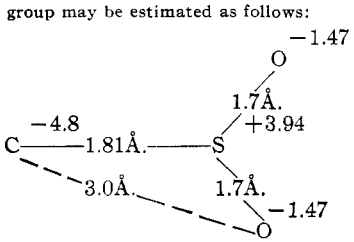
the chemical reactions from which the parallel between sulfone and carbonyl groups has been drawn are ionic reactions. An example is ionization of a hydrogen atom on an adjacent carbon atom.

$$R{-}\underset{X}{\overset{R}{C}}{-}H + :B \rightleftharpoons R{-}\underset{X}{\overset{R}{C^-}}: + BH^+$$

The influence of the substituent X on the course of this reaction, as on many other polar reactions, is undoubtedly due to a combination of two independent effects, a simple electrical effect and resonance or mesomeric interaction. The reaction as written will be favored if either or both effects stabilize the anion more than the undissociated molecule. An electrical effect will accomplish this stabilization if the group X has permanent dipoles with the positive poles directed toward the anionic carbon atom. The carbonyl group and, to a greater extent, the sulfonyl group are each of this character and both would thus favor ionization as indicated.[15] In addition, the unsaturation of the carbonyl group would permit an added mesomeric stabilization by allowing the negative charge to spread out in part to the oxygen atom. Since the evidence presented herein indicates that the sulfonyl group has little or no conjugative properties to a free radical, the close similarity in chemical properties of carbonyl and sulfonyl compounds in ionic reactions suggests that the strong electrical effect of the sulfonyl group is about equal to the combined electrical and resonance effects of the carbonyl group in stabilizing an adjacent carbanion.[15]

In view of these considerations indicating that a charge on an atom can be stabilized both by electrical and by mesomeric or resonance interaction, it would seem that stabilization of a free radical (or an excited) state is a much more nearly unequivocal criterion of mesomeric effects than is stabilization of a polar state.

(15) The direct coulombic stabilization of a carbanion by a sulfone group may be estimated as follows:



$(-4.8 \times 3.94/1.8 + 2(4.8 \times 1.47)/3.0) \times 14.45 = 60$ kcal./mole.

A similar calculation for the carbonyl group gives $(-4.8 \times 1.93/1.54 + 4.8 \times 1.93/2.5) \times 14.45 = 33$ kcal./mole. To attain approximately equivalent stabilization of the carbanion, the carbonyl group must therefore provide at least 25 kcal./mole more resonance stabilization than the sulfone group.

Summary

The copolymerization ratios for methyl vinyl sulfide with styrene and methyl acrylate and for methyl vinyl sulfone with styrene and vinyl acetate have been determined.

The low monomer reactivity of methyl vinyl sulfone supports the view that the sulfur–oxygen bonds are best described as semi-polar rather than covalent double bonds.

Copolymerization data and ultraviolet spectra indicate strong conjugative properties of a sulfide sulfur, interpreted in terms of mesomerism involving expansion of the sulfur octet.

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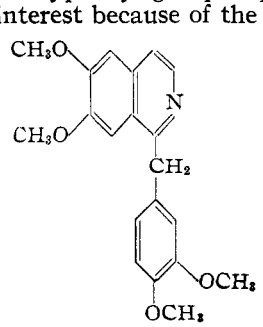
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Synthesis of a Pyridyl Analog of Papaverine

BY C. R. NOLLER* AND M. AZIMA

It has been pointed out previously[1,2] that compounds in which a pyridyl group replaces the dimethoxyphenyl group of papaverine (I) would be of interest because of the effect that the substitution might have on the physiological properties of the compound, and because of the possibility that such compounds might show antimalarial activity. Previous attempts to prepare 1-(α-picolyl)-6,7-methylenedioxyisoquinoline (II) have been unsuccessful, because it has not been possible to dehydrogenate the 3,4-dihydro or the 1,2,3,4-tetrahydro derivative without scission of the side chain.[1,2]



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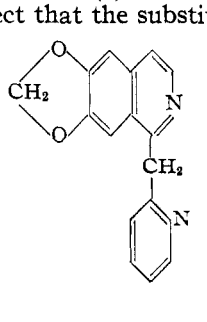

II

Determination of the absorption spectrum of the 3,4-dihydro derivative indicated that it was 1-(α-picolyl)-1,2,3,4-tetrahydro-6,7-methylenedioxyisoquinoline (III), whereas the corresponding phenyl analog is 1-benzyl-3,4-dihydro-6,7-methylenedioxyisoquinoline (IV).[2]

A possible explanation of the greater stability of the exocyclic structure for III as compared with IV is that proton bonding between the two nitrogen atoms is possible for III as indicated in formula V. If such is the case, the β-picolyl deriv-

* Harvard University Visiting Lecturer 1938–1939.

(1) Clemo, McIlwain and Morgan, *J. Chem. Soc.*, 610 (1936).

(2) Bills and Noller, THIS JOURNAL, **70**, 957 (1948).