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3d-Orbital Resonance in Divalent Sulfides. XIV. Free Radical Copolymerization of Ketene Diethylmercaptal with Styrene[1,2]

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Free radical copolymerization reactions of ketene diethylmercaptal (I) and *p*-methylmercaptostyrene (III) with styrene have been carried out. The *Q*-values for I and III are found to be 2.7 and 3.3 respectively, and these and other related observations are discussed in terms of electron-sharing conjugation involving 3d-orbital of sulfur atom.

The ability of sulfur atom to stabilize carbanion has been well known for positively charged sulfur compounds.[4] The major factor for such stabilization is believed to be 3d orbital resonance of sulfur atom. As for divalent sulfides, we have also presented evidence for 3d orbital resonance in the base-catalyzed hydrogen exchange reactions of mercaptals.[5] Thus it seems to be clear that sulfur atom, regardless of its valence state, does stabilize carbanion, presumably by accepting negative charge into its vacant 3d orbital. This ability of

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[2] This is a part of the works submitted to Osaka City University as the Master Thesis by T. Tada.

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[4] C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York (1962).

[5] a) S. Oae, W. Tagaki and A. Ohno, *Tetrahedron*, **20**, 417, 427 (1964). b) *Ibid.*, **20**, 437 (1964).

sulfur atom sharply contrasts with that of oxygen atom which does not have available d-orbital for such stabilization, and moreover α-oxygen group appears to destabilize carbanion.[5a,6]

Meanwhile, in carbonium ion reaction, electron donating conjugation becomes predominant, *i. e.*, nitrogen and oxygen compounds are generally more reactive than the corresponding sulfur analogs. In the free radical reaction, however, our present knowledge is not quantitative enough to predict satisfactorily the course of reaction or the extent of stabilization of an odd electron by sulfur atom. If a free radical center is electrophilic in nature, one might expect that electron-donating conjugation is more dominating over electron-accepting conjugation. In accord with this, the following resonance of the types of (1) and (2) has been suggested by Russell and his coworkers, which accounts for greater reactivity of nitrogen compound than that of the analogous sulfur compound toward the abstraction of α-hydrogen atom:[7]

$$>\ddot{N}-\dot{C}H_2 \longleftrightarrow\ >\dot{N}^{+}-\ddot{C}H_2^{-} \qquad (1)$$

$$-\underset{\cdot\cdot}{\ddot{S}}-\dot{C}H_2 \longleftrightarrow -\underset{\cdot\cdot}{\dot{S}}^{+}-\ddot{C}H_2^{-} \qquad (2)$$

On the other hand, another type of conjugation has been postulated by Price and Oae: electron-sharing conjugation of the type of (3) is conceivable for divalent sulfur compound where sulfur atom accepts odd electron by expanding its valence shell:[4]

$$-\underset{\cdot\cdot}{\ddot{S}}-\underset{|}{\dot{C}}- \longleftrightarrow -\underset{\cdot\cdot}{\dot{S}}^{-}=\underset{|}{C}- \qquad (3)$$

The importance of the latter type of 3d orbital resonance of the sulfur atom has been displayed in several radical reactions, *i. e.*, in free radical addition reaction to the double bond,[8] in peroxide decomposition,[9] and in radical copolymerization reaction,[10] etc. Unfortunately, most of these data are either qualitative or fragmental. Moreover the relative importance of the opposing effects of the type of (2) and (3) should depend on types of reaction, attacking radical and its acceptor.

In the free radical copolymerization reactions, Price and his coworkers found that vinyl sulfide and divinyl sulfide were much more reactive toward growing polystyryl radical than the corresponding oxygen analogs.[10] They treated the data by their *Q-e* scheme.[10c] Although this *Q-e* scheme is purely empirical, it has been shown in a number of cases that larger resonance stabilization of a growing radical seems to be associated with larger *Q* value, and it has been proved to be useful for quantitative estimation of resonance stabilization of a growing radical. For example, the *Q* value of vinyl sulfide is larger than that of vinyl ether, and this has been suggested to be due to the resonance stabilization of the growing radical according to the type of (3). One way to test this concept is to determine the *Q* value of ketene mercaptals, since, just as in the case of base catalyzed hydrogen exchange reactions of mercaptals, the substitution of one additional mercapto group in ketene mercaptal would increase *Q* value substantially over that of vinyl sufide, if *Q* value is a measure of such resonance.

As one of our broad interest in the nature of sulfur bonding, we have now carried out the copolymerization of ketne diethylmercaptal and *p*-methylmercaptostyrene with styrene and compared with those of the corresponding oxygen analogs.

Results and Discussion

All of the compounds, ketene diethylmercaptal (I), ketene diethylacetal (II) and *p*-methylmercaptostyrene (III), were prepared by the known methods as described in the experimental section. Their copolymerizations with styrene were conducted at 60°C with azoisobutyronitrile as the free radical initiator. The monomer, III, gave its copolymer in a satisfactory yield with each monomer ratio. The copolymerization of I was not entirely satisfactory, since, with higher proportion of I, we were unable to isolate any polymer. However, four mixtures (Table 4) gave enough copolymer for the *Q-e* analysis. Unfortunately, the monomer II did not give copolymer. Instead, the only polymer obtained was concluded to be polystyrene, leaving II unreacted (Table 6). This is not surprising in view of the expected increase of negative e-value, probably less than that of I, -2.1, and resulting in an increased difference between the e-values of styrene and the acetal. Perhaps a similar argument cannot be applied to the failure of obtaining copolymer of I in a higher monomer ratio, since, in this case, no polymer, not even polystyrene, could be isolated.

The *Q* and *e* values, thus obtained, are shown in Tables 1 and 2 together with those of the related compounds. Table 1 indicates: (1) The *Q* values of oxygen compounds are very small, especially for ketene diethylacetal (II) which underwent negligible copolymerization. (2) The *Q* values of the sulfone and the silicon compounds are also small. (3) In contrast, the divalent sulfur compounds have large *Q* values. (4) Substitution of one additional mercapto group for vinyl sulfide to ketene diethylmercaptal (I) results in a remarkable increase in *Q* values, much greater

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6) J. Hine, L. G. Mahone and C. L. Liotta, *J. Am. Chem. Soc.*, **89**, 5911 (1967).

7) G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2357 (1964).

8) H. J. Alkema and J. F. Arens, *Rec. trav. chim.*, **79**, 1257 (1960).

9) W. G. Bentrude and J. C. Martin, *J. Am. Chem. Soc.*, **84**, 1561 (1962).

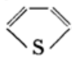
10) a) C. C. Price and J. Zomlefer, *ibid.*, **72**, 14 (1950). b) C. E. Scott and C. C. Price, *ibid.*, **81**, 2672 (1959). c) T. Alfrey and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).

TABLE 1. THE *Q*-*e* VALUES FOR THE COPOLYMERIZATION OF KETENE DIETHYLMERCAPTAL (I) AND OF RELATED COMPOUNDS WITH STYRENE

Compound	*Q*	*e*	Ref.
CH_2=CH-OC_2H_5	0.02	−1.6	11
CH_2=CH-SCH_3	0.34	−1.5	10a
$(CH_2=CH)_2S$	0.68	−1.1	10b
CH_2=C$(OC_2H_5)_2$ (II)	—	—[a]	12
CH_2=C$(SC_2H_5)_2$ (I)	2.70	−2.1	12
CH_2=$CHSO_2CH_3$	0.11	1.2	10a
CH_2=CHSi$(CH_3)_3$	0.03	−0.1	13

a) Only homopolymerization of styrene.

TABLE 2. THE *Q*-*e* VALUES FOR THE COPOLYMERIZATION OF *p*-METHYLMERCAPTOSTYRENE (III) AND OF RELATED COMPOUNDS WITH STYRENE

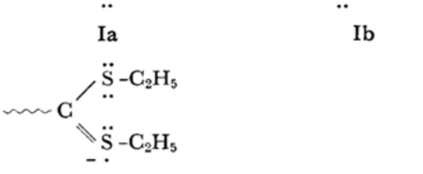
Compound	*Q*	*e*	Ref.
p-CH_3S-C_6H_4-CH=CH_2 (III)	3.29	−1.65	12
C_6H_5-CH=CH_2	1.0	−0.8	17
p-CH_3O-C_6H_4-CH=CH_2	1.0	−1.0	17
p-NO_2-C_6H_4-CH=CH_2	1.86	0.4	17
 -CH=CH_2	3.0	−0.80	17

increase than that from vinyl sulfide to divinyl sulfide.

The smaller *Q* values of the oxygen compound compared with those of the sulfur compounds suggests that in this free radical addition reaction to the double bond the type (2) resonance is less important than the type (3) resonance. In an effort to extend the concept of the electron-sharing conjugation of the type (3), the hydrogen abstraction reaction with various compound substituted at α-carbon atom by heteroatom has been investigated. It was found, however, that the transition state of the hydrogen abstraction reaction by *t*-butoxy or even by phenyl radical is considered to assume a partial carbonium ion character when one judges from the substituent effect on the rates and the negative ρ-value. Thus the order of reactivity of the compounds substituted by hetero atom at α-position is in the order of nitrogen->oxygen->unsubstituted compound.[14] However the situation is different with the mercapto-substituent whose rate-enhancing effect is somewhat larger than that of the corresponding oxygen substituent, despite of the less electron-releasing conjugative effect of mercapto group than that of the corresponding oxygen-compounds. This small anomaly has been suggested to be due to a small contribution of the electron-sharing conjugation of type (3). Meanwhile, ρ-values for the reactions of vinyl phenyl sulfides toward attacking polystyryl radical have been shown to be positive,[15] indicating that the transition state for this addition reaction resembles more carbanion rather than carbonium ion. Unusually low reactivity of the oxygen compounds is consistant with this view, since it has been shown in the carbanion forming reaction that α-alkoxy group even destabilizes the incipient carbanion.[5a,6] Importance of the type (3) resonance can be seen in the small *Q*-values of the sulfone and the silicon compounds which have no available lone electron pair for such conjugation. On the other hand, the abstraction of α-hydrogen atom from the sulfonyl compound has been noted to be extremely difficult.[14] Therefore the moderate Q value of methyl vinyl sulfone also seems to suggest the carbanion type transition state, for sulfonyl group is known to delocalize the charge very effectively.

Incidentally, as one can easily notice, the "electron-sharing" conjugation of the type (3) is possible only with groups bearing lone electron pair such as divalent sulfides that can expand the outer valence shell beyond octet to accomodate an odd electron from the adjacent carbon atom.

We believe that the observations, (3) and (4), together with (1) are good indications of the occurrence of such 3d orbital resonance. The large *Q* value of ketene diethylmercaptal (I) is in accord with the large rate enhancement in the base-catalyzed hydrogen exchange reaction in going from diethyl mercaptal to triethyl orthothioformate.[5a] The resonance stabilization of growing radical of I could be achieved by the contributions of the resonance structures shown in Ia-Ic, *i. e.*, the electron-sharing conjugation of the type (3).



Ia Ib Ic

The newly obtained *Q* value of *p*-methylmercaptostyrene (III) and those of the related compounds are shown in Table 2. Imoto, Kinoshita and their coworkers have developed a method to estimate resonance term in linear free energy relationship in

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11) C. C. Price and T. C. Schwarm, *J. Polymer Sci.*, **16**, 577 (1955).

12) Present work.

13) C. E. Scott and C. C. Price, *J. Am. Chem. Soc.*, **81**, 2670 (1959).

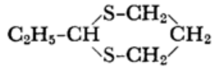
14) K. Uneyama, Y. Nanba and S. Oae, *Yuki Radical Hanno Toronkai* (Symposium on Organic Radical Reaction, Nagoya, 1967, Unpublished work.

15) K. Tsuda, S. Kobayashi and T. Otsu, *J. Polymer Sci.*, submitted: T. Otsu, *Iokagobutsu Toronkai* (Symposium on Sulfur Compounds), Osaka, 1967.

the copolymerization of styrene.[16] Their method suggests the Q value of III to be unusually high. So is the value of 2-vinylthiophene. A likely explanation would be that while a hetero atom combined directly to vinyl double bond could destabilize growing radical by either inductive or lone electron-pair repulsion or by both, the removal of the hetero atom away from the reaction center, for example to the *p*-position of styrene, definitely reduces such effect, and hetero atom, in turn, would display more effective conjugation through phenyl ring, mobilizing an odd electron from its lone pair.

Table 3 shows the UV spectra of I together with those of the related compounds. The large red shift in divinyl sulfide than in vinyl sulfide has been suggested to be partly due to the "through conjugation".[4a] Although such through-conjugation is impossible, similar order of red shift is found in I. This would suggest a non-bonding interaction between the two sulfur atoms in I in the photo-excited state.[5b]

TABLE 3. ULTRAVIOLET SPECTRA OF KETENE DIETHYLMERCAPTAL AND OF THE RELATED SULFIDES

Compound	Solvent	λ_{max}, mμ	log ε	Ref.
$CH_2=CH-SCH_3$	EtOH (95%)	230	4.20	10a
		240	4.00	10a
$(CH_2=CH-)_2S$	Dioxane	240	3.90	10b
		255	3.90	10b
$CH_2=C(S-C_2H_5)_2$ (I)	EtOH	234	3.53	12
		249	3.60	12
$C_2H_5-CH(S-C_2H_5)_2$	EtOH	231	2.92	5b
	EtOH	231	2.71	5b
		250	2.79	5b

Experimental

Preparation of Materials. *Ketene Diethylmercaptal* (I)[18] was prepared by the acid catalyzed elimination of ethyl mercaptan from triethyl orthothioacetal (bp 121°C/10 mm), 80°C/15 mmHg., n_D^{20} 1.5304 (lit., 1.5306[18]).

Ketene Diethylacetal (II)[19] was prepared by the elimination reaction of triethyl β-bromoorthoacetate (bp 80°C/10 mmHg), with dispersed sodium metal in anhydrous benzene, bp 68°C/100 mmHg (lit., 68°C/100 mmHg[19]), n_D^{27} 1.4095 (lit., 1.4110[19]).

p-Methylmercaptostyrene was prepared starting from *p*-bromoacetanilide. *p*-Bromoacetanilide was converted to *p*-bromothioanisole by the diazotization, followed by the reaction with methyl mercaptan, bp 103—105°C/14 mmHg, mp 40°C (lit. mp 40°C[20]). *p*-Bromothioanisole was converted to Grignard reagent in tetrahydrofuran and reacted with acetaldehyde. The resulting alcohol was dehydrated with potassium hydrogen sulfate at 260°C under vacuum to give *p*-methylmercaptostyrene, bp 82°C/3 mmHg. (Lit. bp 83—85°C/3 mm[21]), identified by IR, and NMR spectra.

TABLE 4. COPOLYMERIZATION OF KETENE DIETHYLMERCAPTAL (M_2) WITH STYRENE (M_1)[a]

M_2[b]	Reaction time, hr	Conversion, %[c]	S%[d]	C%	H%	m_2[e]
0.200	30	12.3	9.64	82.58	7.86	0.167
0.300	30	10.1	13.35	78.59	7.95	0.239
0.400	30	9.5	16.62	74.84	7.98	0.258
0.500	30	7.2	19.12	72.58	8.14	0.322
0.600	30	f				
0.700	30	f				
0.800	30	f				

$r_1=1.046$, $r_2=0.1587$, $Q=2.79$, $e=-2.1$[g]

a) The other two runs gave almost the same results.
b) Mole fraction in monomer mixture. Total 0.08—0.05 mol of monomer and 35 mg of azoisobutyronitrile.
c) Weight % of the dried copolymer precipitated from methanol.
d) Used for the estimation of Q and e.
e) Mole fraction of I in copolymer calculated from S %.
f) No polymer.
g) The other set of Q-e values were eliminated based on the fact that they did not accord with the reported value of k_{11}(=176 l/mol/sec, 60°C)[22] for styrene polymerization.

TABLE 5. COPOLYMERIZATION OF *p*-MERCAPTOSTYRENE (M_2) WITH STYRENE (M_1)[a]

M_2	Reaction time, hr	Conversions, %	S%	m_2
0.250	0.75	5.67	8.56	0.317
0.333	0.75	5.43	10.32	0.393
0.500	0.75	7.13	13.16	0.527
0.667	0.75	7.58	16.48	0.700
0.750	0.75	8.12	17.32	0.749

$r_1=0.596$ $r_2=0.812$ $Q=3.29$ $e=-1.65$[b]

a) Apply the same foot notes of (a) to (e) in Table 4 to this table.
b) The other set was $Q=0.85$ and $e=+0.05$. The positive e value is unlikely for styrene derivative.

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16) M. Imoto, M. Kinoshita and M. Nishigaki, *Makromol. Chem.*, **94**, 238 (1966).
17) C. C. Price, *J. Polym. Sci.*, **3**, 772 (1948).
18) L. C. Rinzew, J. Stoffelsma and J. F. Arens, *Rec. Trav. Chim.*, **78**, 355 (1959).
19) P. M. Walters and S. M. McElvain, *J. Am. Chem. Soc.*, **62**, 1482 (1940).
20) E. A. Nodiff, S. Lipschutz, P. N. Craig and M. Gordon, *J. Org. Chem.*, **25**, 60 (1960).
21) G. B. Bachman and C. L. Carlson, *J. Am. Chem. Soc.*, **73**, 2857 (1951).
22) M. S. Matheson, E. E. Auer, E. B. Bevilacque and E. J. Hart, *J. Am. Chem. Soc.*, **73**, 1700 (1951).

Table 6. Copolymerization of ketene diethylacetal (M_2) with styrene (M_1)

M_2[a]	Reaction time, hr	Conversion,	C%	H%	(C+H) %[b]
0.125	3	15.8	92.15	7.79	99.94
0.250	3	15.5	92.10	7.72	99.82
0.375	3	13.2	91.86	7.68	99.54
0.500	3	10.7	90.93	7.80	98.73
0.625	3	11.5	92.49	7.82	100.31
0.750	3	10.2	91.53	7.73	99.26
0.875	3	8.4	91.30	7.67	98.97

a) Each tube contained 35 mg of azoisobutyronitrile.

b) These values indicates that there was practically no copolymerization.

Copolymerization with Styrene. The reaction mixture was prepared by mixing styrene with each monomer and azoisobutyronitrile and sealed under high vacuum. The polymerization was carried out by shaking the sealed tubes in a constant temperature bath (60°C). Polymer was isolated by pouring the contents of the tube into 200 m*l* of cold methanol. The dried precipitate was dissolved in benzene again and reprecipitated in cold methanol. Dried pure sample, thus made was subjected to analysis and the results are listed in Tables, 4, 5 and 6.

From the data in Table 4 the copolymerization ratios, r_1 and r_2 were estimated by the intersection method using Eq. (4). The Q and e values were then calculated using Eqs. (5) and (6)[10c] and assuming the Q and e values for styrene as 1.00 and −0.8, respectively.[17]

$$r_2 = \frac{M_1}{M_2}\left[\frac{\mathrm{d}M_2}{\mathrm{d}M_1}\left(1+\frac{M_1}{M_2}r_1\right)-1\right] \tag{4}$$

$$r_1 = (Q_1/Q_2)e^{-e_1(e_1-e_2)} \tag{5}$$

$$r_2 = (Q_2/Q_1)e^{-e_2(e_2-e_1)} \tag{6}$$

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