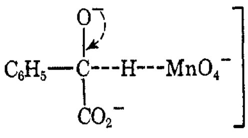
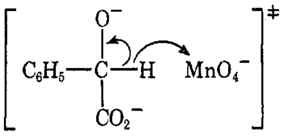
Although the kinetic data presented are consistent with both Scheme I and II, the activated complex in Scheme I could be represented by XIV and the activated complex for Scheme II could be represented by XV. In view of the close analogy between Scheme I and II, the available data for the permanganate oxidation of alkoxide ions and the anions of aldehyde hydrates, it is not possible to differentiate between the hydride transfer mechanism and the hydrogen atom mechanism.


XIV


XV

**Registry No.**—I, 769-61-9; I, 4-Br, 25296-24-6; I, 4-Cl, 25296-25-7; I, 4-CH$_3$, 25356-01-8.

**Acknowledgment.**—We would like to thank Professor S. S. Kuwahara of this department and Mr. A. A. Kamego[42] for obtaining the pmr spectra.

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# A Novel Single-Step Sulfone Synthesis

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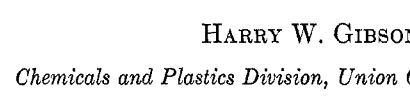
A recently reported synthesis of sulfones from olefins and sulfur dioxide in the presence of formic acid–tertiary amine "adducts" has been investigated. The reaction appears to be limited to monosubstituted olefins bearing an electron-withdrawing group. The sulfones are usually accompanied by the corresponding disulfides, which can be the major products under certain conditions. Disubstituted terminal olefins do yield disulfides. The solvent "adducts" were found to be azeotropes; in fact formic acid *per se* is not required, only formate ion. Mechanistically the intermediacy of sulfoxylic acid (H$_2$SO$_2$, formed by reduction of sulfur dioxide) in the generation of a sulfinic acid from the olefin is confirmed. The sulfone is formed by addition of the sulfinic acid to a second mole of olefin. Deuterium tracer work indicates that exchange of the protons $\alpha$ to the sulfinyl group occurs in the intermediate sulfinic acid. The deuterium tracer work also militates against a termolecular reaction of olefin, sulfur dioxide, and formate ion leading in one step to sulfinic acid and thus supports stepwise generation of sulfoxylic and sulfinic acids. There are several feasible mechanistic pathways for disulfide formation. The most likely route consists of reaction of elemental sulfur (formed by formate reduction of sulfur dioxide) and a mercaptan (probably arising *via* disproportionation of the corresponding sulfinic acid).

A recent patent reported that reaction of certain terminal olefins with sulfur dioxide in the presence of "adducts" of formic acid and trimethyl- or triethylamine affords sulfones in 13–63% yield with evolution of carbon dioxide.[1a] The report states that "adducts"[1b] of formic acid and a variety of other tertiary amines are not as effective. Formic acid and formamides were also utilized.



$$2\ \overset{R_1}{\underset{R_2}{>}}C{=}CH_2 + SO_2 \xrightarrow{HCOOH} R_1\underset{R_2}{\underset{|}{C}}HCH_2SO_2CH_2\underset{R_2}{\underset{|}{C}}HR_1$$

1 2

**a**, R$_1$ = H; R$_2$ = CONH$_2$
**b**, R$_1$ = H; R$_2$ = COOH
**c**, R$_1$ = H; R$_2$ = CN
**d**, R$_1$ = H; R$_2$ = COOCH$_3$
**e**, R$_1$ = CH$_3$; R$_2$ = COOCH$_3$
**f**, R$_1$ = CH$_3$; R$_2$ = CONH$_2$

In view of the intriguing nature of this transformation, the lack of evidence for mechanistic speculations and our interest in the chemistry of formic acid,[2] we have examined the scope and mechanism of the reaction.

**The Reaction.**—"Adducts" of formic acid and tertiary amines have been used as reducing media in other processes.[3] They have also seen use in other applications.[4] Examination of the "adducts" of formic acid with trimethyl- and tributylamine by vpc, ir, and pmr revealed that no new covalent compounds were present. The only compounds present were formic acid and the tertiary amine. The molar ratio of the two components varied from amine to amine. Moreover, for a given amine the composition varied with distillation pressure. These data are interpreted as indicating that the "adducts" are really azeotropes. This is substantiated by the fact that synthetic mixtures of the two components are as effective in the reaction as the distilled materials.

Using acrylamide (**1a**) as starting material and the formic acid–trimethylamine azeotrope (3.0:1.0), the optimum temperature under our reaction conditions was found to be 100° at which a 61% yield of bis(2-carboxamidoethyl) sulfone (**2a**) was obtained. Variation of the formic acid–trimethylamine ratio appeared to have little effect on yield. The tertiary amines were not unique as cosolvents with the formic acid. Pyridine, secondary and primary amines, formamides, and ammonium and sodium formates were also satisfactory. These results suggested that the active species in the solvent was formate ion. This view was supported by the lack of reaction with neat formic acid, neat fromamide, and acetic acid–trimethylamine (3.0:1.0). Indeed solutions of sodium or ammonium formate in acetic acid were suitable (55% yield under conditions

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(1) (a) Farbenfabriken Bayer A.-G., German Patent 1,222,048 (1966); *Chem. Abstr.*, **65**, 13545e (1966). (b) A referee states that in German "adduct" means "loose addition product without forming covalent bonds" and in this context is correct (*vide infra*).

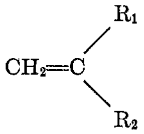
(2) H. W. Gibson, *Chem. Rev.*, **69**, 673 (1969).

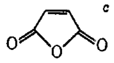
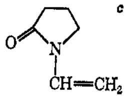
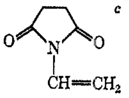
(3) (a) M. Sekiya and K. Ito, *Chem. Pharm. Bull.*, **12**, 677 (1964); (b) M. Sekiya, Y. Harada, and K. Tanaka, *ibid.*, **15**, 833 (1967). See ref 2 for discussion of these and other uses of formic acid media as reducing agents.

(4) M. Sekiya, M. Tomic, and N. J. Leonard, *J. Org. Chem.*, **33**, 318 (1968). See also ref 2.

TABLE I

SCOPE OF THE REACTION WITH OLEFIN I

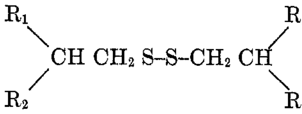


| $R_1$ | $R_2$ | Conditions (Table VII) | Product | % yield |
|---|---|---|---|---|
| H | $CONH_2$ | A | **2a**[d] | 61 |
| H | $CONH_2$ | B[a] | **3a**[e] | 44 |
| H | COOH | A[a] | **2b**[f] | 44 |
| H | COOH | A | **2b** | 6 |
| | | | **3b**[g] | 20 |
| H | $COOCH_3$ | A | **2d**[h] | 52 |
| | | | **3c**[i] | 5 |
| H | CN | A | **2c**[j] | 12 |
| H | $SO_2CH{=}CH_2$ | A[a] | **4**[k] | 80 |
| $CH_3$ | $COOCH_3$ | C | **3d**[l] | 34 |
| H | $(CH_2)_7CH_3$ | C[b] | Sulfur | 81 |
| H | $C_6H_5$ | A[b] | Sulfur | |
| H | $COCH_2CH_3$ | D[b] | | |
| H | $CONH_2$ | A[a] | **2a** | 19 |
| H | $C_6H_5$ | | | |
| $CH_3$ | $COOCH_3$ | A[a] | | |
| H | $(CH_2)_5CH_3$ | | | |
| $ClCH{=}CCl_2$[c] | | A[b] | Sulfur | 53 |
| *trans*-$HOOCCH{=}CHCOOH$[c] | | A[a,b] | | |
| $CH_3CH{=}CHCHO$[c] | | C | | |
|  [c] | | A | Sulfur,<br>succinic acid | 5 |
|  [c] | | A[a] | Sulfur | 31 |
|  [c] | | A[a] | Sulfur | 78 |

[a] 3-hr addition. [b] Two-phase reaction. [c] Olefin structure in entirety. [d] Mp 228.5–229.5° ($H_2O$); lit.[1] mp 228°. *Anal.* Calcd for $C_6H_{12}N_2SO_4$: C, 34.60; H, 5.81; N, 13.46; S, 15.40. Found C, 34.68; H, 5.84; N, 13.44; S, 15.32. [e] Mp 176.0–178.0° ($H_2O$). *Anal.* Calcd for $C_6H_{12}N_2S_2O_2$: C, 34.59; H, 5.81; N, 13.45; S, 30.79. Found: C, 34.62; H, 5.80; N, 13.39; S, 30.85. [f] Mp 223.0–223.5° ($H_2O$); lit. mp 222–224° [N. Gunderman and C. Burba, *Chem. Ber.*, **94**, 2157 (1961)]; 223–225° [R. Dahnborn, *Acta Chem. Scand.*, **5**, 690 (1951)]; 220°.[1a] [g] Mp 156.0–157.5° ($H_2O$); lit. mp 154–155° [R. Dahnborn, *Acta Chem. Scand.*, **5**, 690 (1951); C. Buess, *J. Amer. Chem. Soc.*, **77**, 6613 (1955)]. *Anal.* Calcd for $C_6H_{10}S_2O_4$: C, 34.27; H, 4.79; S, 30.50. Found: C, 34.37; H, 4.76; S, 30.40. [h] Mp 111.8–112.5° ($H_2O$); lit. mp 115° [J. MacGregor and C. Pugh, *J. Chem. Soc.*, 736 (1950)]. *Anal.* Calcd for $C_8H_{14}SO_6$: C, 40.33; H, 5.92; S, 13.46. Found: C, 40.42; H, 5.88; S, 13.60. [i] Yellow liquid, analyzed after bicarbonate washing and drying; lit. yellow oil, no bp given; S, 27.9 [R. Pierson, A. Costanza, and W. Weinstein, *J. Polym. Sci.*, **17** 221 (1955)]. *Anal.* Calcd for $C_8H_{14}S_2O_4$: C, 40.32; H, 5.92; S, 26.91. Found: C, 40.46; H, 5.89; S, 26.78. [j] Mp 87.5–88.0° ($H_2O$); lit. mp 86°,[1a] 84° [J. Alexander and H. McCombie, *J. Chem. Soc.*, 1913 (1931)]. *Anal.* Calcd for $C_6H_8N_2SO_2$: C, 41.84; H, 4.68; N, 16.27; S 18.62. Found C, 41.86; H, 4.61; N, 16.12; S, 18.55. [k] Mp >330°, dec 300° (dil $HNO_3$); lit. mp >370°, dec 330° [W. Parham, H. Wynberg, and F. Ramp, *J. Amer. Chem. Soc.*, **75**, 2065 (1953)]. [l] Pale yellow liquid, bp 103–105° (0.08 mm). *Anal.* Calcd for $C_{10}H_9S_2O_4$: C, 45.09; H, 6.81; S, 24.08. Found: C, 44.91; H, 6.71; S, 24.16.

equivalent to those mentioned above). Because of the relative acidities of acetic and formic acid (p$K_a$ of 4.75 *vs.* 3.75[5]) very little formic acid would be present in these solutions. Thus, while formic acid *per se* is not required, the formate ion is required.

In the case of acrylamide (**1a**) the solvent:substrate ratio was of consequence using formic acid–trimethylamine (3.0:1.0). In a run utilizing twice the normal amount of solvent, a new product was isolated in about the same yield as the sulfone **2a** under normal conditions. On the basis of spectral and elemental analyses this material proved to be disulfide **3a**. The formation of disulfides was not reported in the patent literature, although in some cases unidentified compounds were isolated.[1a] When acetic acid–ammonium formate was employed, no crossover to disulfide was observed at higher dilution, and the sulfone isolated was of higher purity than that obtained with formic acid–trimethylamine. Other olefins did not exhibit this crossover effect. It appears to be peculiar to the acrylamide reaction in formic acid–trimethylamide.



$$(R_1)(R_2)CHCH_2S{-}S{-}CH_2CH(R_1)(R_2)$$

**3a**, $R_1$ = H; $R_2$ = $CONH_2$
**b**, $R_1$ = H; $R_2$ = COOH
**c**, $R_1$ = H; $R_2$ = $COOCH_3$
**d**, $R_1$ = $CH_3$; $R_2$ = $COOCH_3$
**e**, $R_1$ = $CH_3$; $R_2$ = $CONH_2$

The generality of the reaction was tested using a variety of olefins. These are summarized in Table I.

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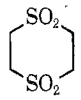
[5] "Handbook of Chemistry and Physics," 41st ed, Chemical Rubber Co., Cleveland, Ohio, 1960, p 1744.

Of the olefins tested only acrylonitrile, acrylic acid, methyl acrylate, and acrylamide yielded sulfones **2**. Divinyl sulfone yielded **4**. Except for acrylonitrile and divinyl sulfone, disulfides **3** accompanied the sulfone products. Methyl methacrylate (**1e**) yielded only disulfide **3d**. In many cases where the olefins were unreactive, elemental sulfur was formed. Structural requirements of the olefin for sulfone formation appear to dictate that it be a monosubstituted ethylene bearing one of the following electron-withdrawing groups: CN, $CONH_2$, COOR, $SO_2R$. These structural requirements are similar to those stated previously[1a] with one important exception. It was reported that methacrylamide (**1f**) yielded (13%) sulfone **2f**. It was then concluded that 2,2-disubstituted terminal olefins are capable of undergoing the sulfone-forming reaction.[1a] However, our finding that methyl methacrylate (**1e**) yields not the corresponding sulfone **2e**, but rather disulfide **3d** casts doubt upon this conclusion. In the absence of any evidence for the assigned sulfone structure, it is possible that the compound previously isolated was disulfide **3e**. We did not prepare either of these compounds. It should be pointed out that C, H, and N elemental analyses will not distinguish between corresponding sulfones and disulfides (see Table I); a sulfur analysis is required. It, therefore, appears doubtful that disubstituted terminal olefins can serve as sulfone precursors in this process.


**4**

The physical properties and elemental analyses of the sulfones **2** and disulfides **3** are presented in Table I. Bis(2-carbomethoxypropyl) disulfide (**3d**) exhibited two peaks of 1.0:1.5 area ratio (in order of elution) on vpc. Separation of the components afforded two liquids with identical infrared spectra but for minor shifts and with pmr spectra identical except for small (~0.1 ppm) chemical shift differences. A distilled mixture of the liquids was subjected to elemental analysis which supported the contention that they were the *meso* and *dl* isomers of **3d**.

The pmr spectra were diagnostic for structure of the products resulting from reaction of the acrylic compounds. The sulfones showed somewhat distorted AX triplets at δ 3.1–3.2 and 3.7–3.8 assigned to methylene groups adjacent to the CN or COR and $SO_2$ groups, respectively. Sulfone **2b** had an eight-line $A_2B_2$ pattern. On the other hand, the disulfides all exhibited more complex splitting patterns due to the more nearly equal chemical shifts of the two sets of methylene protons. In disulfide **3a** a broad singlet was observed; with **3b** and **3c**, eight-line multiplets typical of $A_2B_2$ systems were recorded. No attempt was made to analyze these signals. Pmr spectral data are summarized in Table II.

The sulfones possessed typical peaks at about 1300 and 1150 $cm^{-1}$ in the infrared (S–O stretch).

The mass spectra of sulfones **2a**, **2c**, and **2d** and disulfide **3a** were recorded. Sulfone **2a** appears to be noteworthy in that its spectrum (Table III) does not contain a peak corresponding to a parent ion (*m/e* 208), and it does not seem to fragment initially at the sulfone linkage. Instead, the molecule appears to undergo fragmentation piece by piece as evidenced by the series of lower mass peaks. Scheme I is a proposed rationalization of its fragmentation pattern.

TABLE II

PMR SPECTRA[a]

| Compd | Chemical shift, δ |
|---|---|
| **2a** | 3.18 (2 H, t, 7[b]), 3.80 (2 H, t, 7), ~7 (2 H, s) |
| **2b**[c] | 3.21 (2 H, t, 6), 3.89 (2 H, t, 6) |
| **2c** | 3.20 (2 H, t, 7), 3.74 (2 H, t, 7) |
| **2d** | 3.08 (2 H, t, 7), 3.69 (2 H, t, 7), 3.91 (3 H, s) |
| **3a** | 2.63 (broad s) |
| **3b**[c] | 3.08 (8-line m) |
| **3c** | 2.85 (4 H, 8-line m), 3.71 (3 H, s) |
| **3d**[d] | 1.25 (3 H, d, 6), 2.82 (3 H, m), 3.68 (3 H, s) |

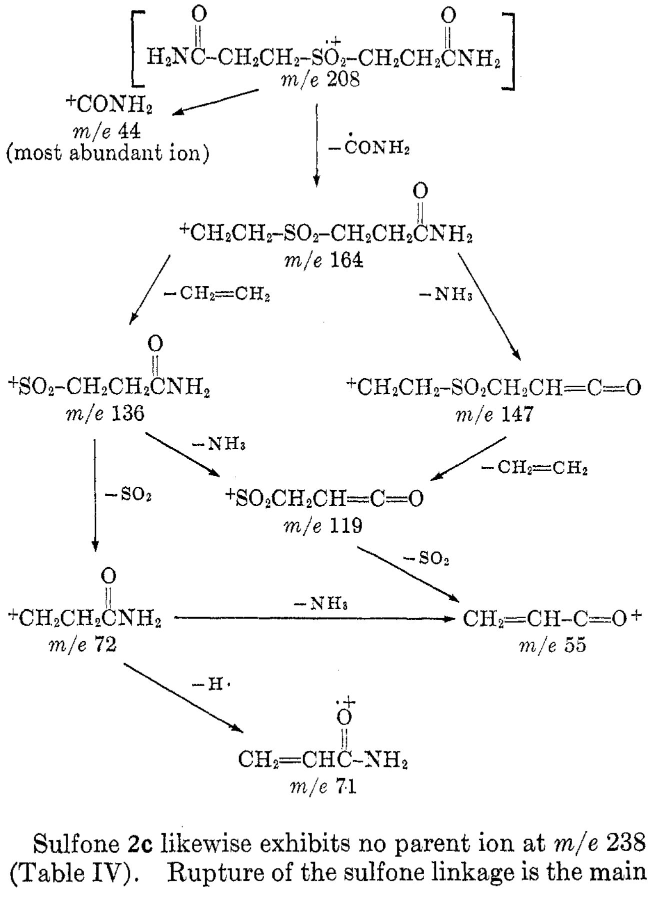
[a] Recorded in trifluoroacetic acid (25% w/w) unless otherwise indicated. [b] Coupling constants in hertz. [c] Recorded in pyridine (25% w/w). [d] Recorded in carbon tetrachloride (25% w/w).

TABLE III

MAJOR PEAKS IN MASS SPECTRUM OF **2a**

| *m/e* | Rel abundance | *m/e* | Rel abundance |
|---|---|---|---|
| 16 | 13 | 55 | 98 |
| 17 | 29 | 56 | 26 |
| 18 | 57 | 64 | 21 |
| 26 | 28 | 71 | 84 |
| 27 | 65 | 72 | 30 |
| 28 | 41 | 73 | 32 |
| 30 | 13 | 119 | 13 |
| 43 | 20 | 136 | 10 |
| 44 | 100 | 147 | 1.8 |
| 45 | 16 | 164 | 4.2 |

SCHEME I



Sulfone **2c** likewise exhibits no parent ion at *m/e* 238 (Table IV). Rupture of the sulfone linkage is the main

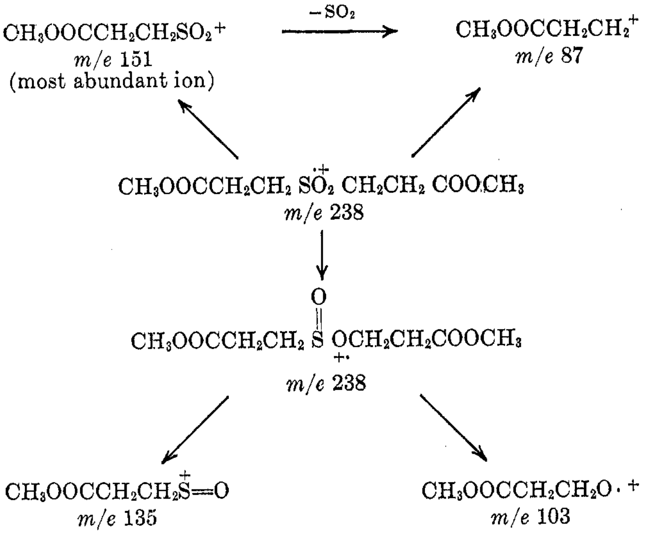
TABLE IV

MAJOR PEAKS IN MASS SPECTRUM OF **2c**

| m/e | Rel abundance | m/e | Rel abundance |
|---|---|---|---|
| 28 | 12 | 103 | 18 |
| 55 | 40 | 135 | 53 |
| 59 | 36 | 147 | 43 |
| 87 | 45 | 151 | 100 |
| 88 | 11 | | |

cleavage. In addition, postionization rearrangement to the sulfinate ester, as has previously been observed in sulfones,[6] seems to occur in this system, on the basis of peaks at *m/e* 135 and 103. Scheme II is consistent with the observed spectrum for sulfone **2c**.

SCHEME II



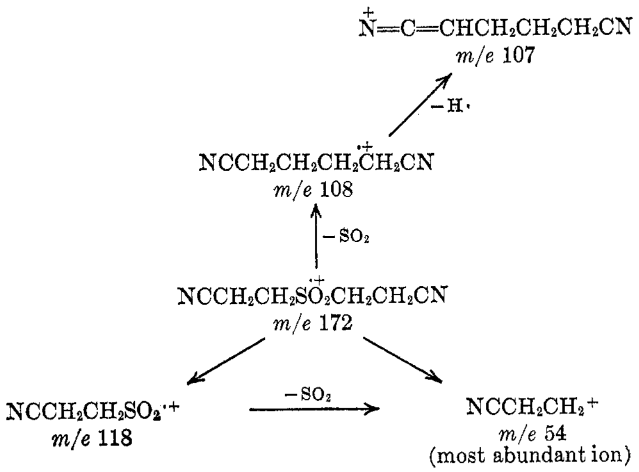
The mass spectrum of sulfone **2d** (Table V) does contain a molecular ion peak at *m/e* 172. Again, sulfone cleavage predominates to give fragments *m/e* 118 and 54. Accurate mass measurements militate against *m/e* 118 arising from loss of 2 mol of hydrogen cyanide. This is corroborated by the lack of a peak at *m/e* 145 due to loss of 1 mol of hydrogen cyanide from the parent ion. Extrusion of sulfur dioxide is probably the origin of the *m/e* 108 peak, which is too large to be an isotope peak of *m/e* 107. The loss of a hydrogen atom is characteristic of alkyl nitriles and the formation of *m/e* 107 from *m/e* 108 is substantiated by a metastable cusp between *m/e* 108 and 109.[7] These fragmentations are depicted in Scheme III.

TABLE V

MAJOR PEAKS IN MASS SPECTRUM OF **2d**

| m/e | Rel abundance | m/e | Rel abundance |
|---|---|---|---|
| 28 | 9 | 107 | 2.5 |
| 54 | 100 | 108 | 0.6 |
| 55 | 66 | 109 | 0.2 |
| 68 | 10 | 118 | 2.7 |
| | | 172 | 2.2 |

SCHEME III



The mass spectrum of disulfide **3a** (Table VI) contains a parent ion peak (*m/e* 208). Disulfide (S–S) cleavage with hydrogen transfer, possibly *via* a four-centered reaction, leads to *m/e* 105 and 103. A unique feature of the spectrum is the lack of major fragments greater than half the size of the parent ion. Peaks at *m/e* 71, 72, and 55 may have arisen by loss of hydrogen sulfide and ammonia from the *m/e* 105 species. Rationalization of the observed spectrum is given in Scheme IV.

TABLE VI

MAJOR PEAKS IN MASS SPECTRUM OF **3a**

| m/e | Rel abundance | m/e | Rel abundance |
|---|---|---|---|
| 17 | 14 | 58 | 14 |
| 18 | 27 | 59 | 37 |
| 26 | 21 | 60 | 15 |
| 27 | 44 | 61 | 29 |
| 28 | 31 | 64 | 13 |
| 43 | 27 | 70 | 13 |
| 44 | 74 | 71 | 100 |
| 45 | 25 | 72 | 62 |
| 46 | 14 | 73 | 10 |
| 47 | 35 | 88 | 21 |
| 52 | 14 | 101 | 52 |
| 53 | 19 | 103 | 49 |
| 54 | 12 | 104 | 17 |
| 55 | 91 | 105 | 70 |
| 56 | 18 | 106 | 12 |
| | | 208 | 8.4 |

**The Mechanism.**—The following mechanism was proposed[1a] to account for sulfone formation.

$$SO_2 + HCOOH \longrightarrow \underset{\mathbf{5}}{HOSOH} + CO_2 \qquad (1)$$

$$H_2SO_2 + \mathbf{1} \longrightarrow R_1\underset{R_2}{\underset{|}{C}}HCH_2SO_2H \qquad (2)$$

**6a**, $R_1 = H$; $R_2 = CONH_2$
**b**, $R_1 = CH_3$; $R_2 = COOCH_3$

$$\mathbf{6} + \mathbf{1} \longrightarrow \mathbf{2} \qquad (3)$$

Our initial efforts in the mechanistic study of this multistage reaction were directed at the proposed addition of sulfinic acid **6** to olefin **1** (eq 3). Sulfinic acids are reported to react with alkyl halides and sulfates and

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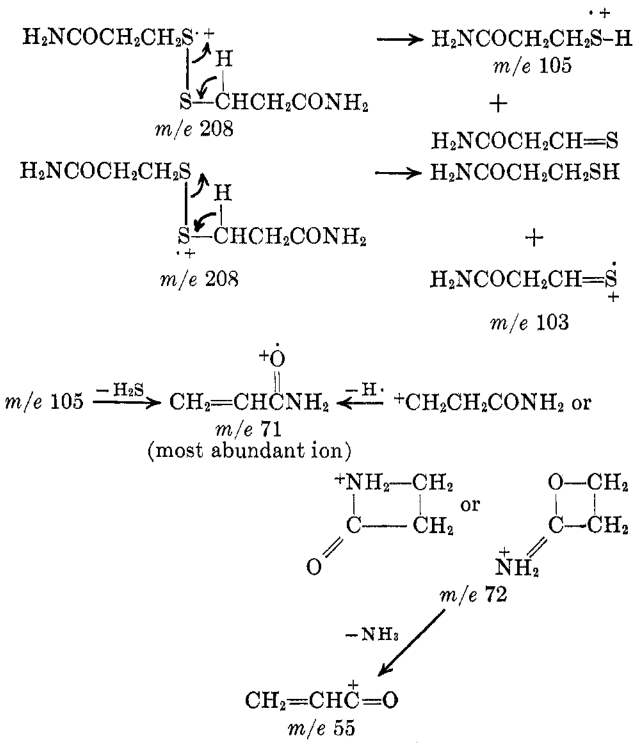
[6] S. Meyerson, H. Drews, and E. K. Fields, *Anal. Chem.*, **36**, 1294 (1964).

[7] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1964, p 112.

SCHEME IV



activated aromatic halides, yielding sulfones.[8] In addition, Russian workers have published an account of the preparation of sulfones from sodium arenesulfinates and acrylic acid derivatives in the presence of weak acids.[9] Thus, it appeared that the addition in question was feasible. Using sodium benzenesulfinate and acrylamide (**1a**) under our original reaction conditions (minus sulfur dioxide), a 90% yield of the expected sulfone **9** was isolated.

$$\mathrm{PhSO_2Na} + \mathbf{1a} \longrightarrow \underset{\mathbf{9}}{\mathrm{PhSO_2CH_2CH_2CONH_2}}$$

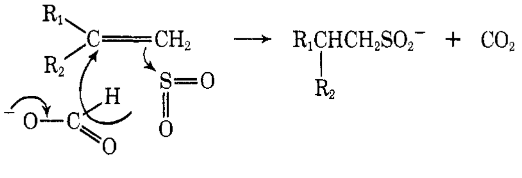
More significantly, it was of interest to determine whether the particular aliphatic sulfinic acid **6** proposed above as an intermediate would add to acrylamide (**1a**). Reductive cleavage of **9** led to a mixture of the desired **6a** (as its sodium salt) and sodium benzenesulfinate in a 2:1 ratio. Treatment of acrylamide (**1a**) with this mixture under normal reaction conditions led as expected to **9** along with the desired symmetrical sulfone **2a**, the product of addition of the sulfinic acid **6a** to acrylamide (**1a**). These experiments firmly demonstrate the feasibility of eq 3 as a route to sulfone **2** from sulfinic acid **6** and olefin **1**.

Next, to distinguish between occurrence of sulfoxylic acid (**5**) as a discrete intermediate as indicated in eq 1 or formation of sulfinic acid **6a** *via* some one-step reaction, tracer experiments using sodium formate-*d* were carried out.

Considering the first possibility, if sulfoxylic acid (**5**) is a discrete intermediate, it would be expected to exchange its protons with the reaction medium. Likewise, the sulfinic acid **6a** is quite acidic[10] and also would be expected to exchange its acidic proton with the solution. Thus, if formate-*d* were the "hydride" source in eq 1, the proportion of deuterium appearing in the methylene groups β to the sulfonyl group in sulfone **2a** would be a function of the amount of solvent employed.

However, if sulfinic acid **6a** is formed by a concerted termolecular process involving direct hydride transfer from formate ion to the tertiary carbon of the olefin, as depicted in Scheme V the protons β to the sulfonyl group in sulfone **2a** should contain 25% deuterium if formate-*d* is used, regardless of the amount of solvent.

SCHEME V



The possibility of exchange of any of the methylene protons in sulfone **2a**, either in the reaction or during work-up and analysis, was precluded by the following results. The sulfone **2a** was heated at 100° in the presence of sodium formate, acetic acid, and deuterium oxide. The sulfone was recovered and pmr analysis, using pivalic acid as an internal standard, revealed that no exchange took place at the methylene positions. Next, the sulfone **2a** was subjected to actual reaction conditions (except for the absence of sulfur dioxide) using sodium formate and acetic acid-$d_4$. Once again pmr analysis showed no exchange of methylene protons. To eliminate the possibility of exchange during pmr analysis, a sample was heated in trifluoroacetic acid-*d* (solvent for pmr analyses) for a few minutes and allowed to stand 24 hr prior to examination. No exchange of the methylene protons took place.

In a preparative experiment in which both sodium formate-*d* and acetic acid-$d_4$ were used, the pmr spectrum of the resultant sulfone showed broadened signals due to the protons α to the sulfonyl group and those β in a 1.15:1.00 ratio, respectively. If the mechanism of formation of sulfinic acid **6a** shown in Scheme V were correct and the methylene protons did not exchange, an α:β ratio of 1.45:1.00 would obtain; with exchange of the methylene protons α to the sulfinyl group an α:β ratio of 1.50:1.00 would result. It is apparent that the termolecular mechanism is not operative. If the mechanism in eq 1–3 is correct and the methylene protons α to the sulfinyl did not exchange, the α:β ratio would be 1.41:1.00. Assuming that the olefin exchanges only the amide NH protons, the results indicate that sulfinic acid **6a** undergoes exchange of protons. Since the protons α to the carbonyl group in sulfone **2a** do not exchange under reaction conditions, it is unlikely that those of the sulfinic acid **6a** do so. Thus, it appears that the protons α to the sulfinyl group exchange, either in the sulfinic acid or its anion. If complete exchange of these protons and those of the amide group is assumed, the area ratio of signals for protons α and β is statistically calculated to be 1.00:1.00, respectively.

The preparative reaction was carried out using sodium formate-*d* in the normal amount of acetic acid and in one-half that amount. In neither case was the ratio of protons α to β in **2a** 1.33:1.00. Thus, the termolecu-

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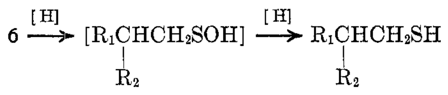
[8] R. Otto, *Chem. Ber.*, **13**, 1272 (1880); H. Gilman, "Organic Chemistry, An Advanced Treatise," Vol. I, Wiley, New York, N. Y., 1958, p 874.

[9] V. Mikhailova, N. Borinsova, and D. Stankevich, *J. Org. Chem. USSR*, **2**, 1437 (1966).

[10] W. E. Truce and A. M. Murphy, *Chem. Rev.*, **48**, 69 (1951).

lar mechanism must be discarded, since it would not involve free deuterons in solution to cause exchange at $\alpha$. One would expect from statistical calculations that as a result of exchange of $\alpha$ protons, the ratios of $\alpha$ to $\beta$ in both of these reactions would be about 1.00:1.00. This is precisely what has been observed. These results lend support to eq 1 and 2 of the proposed mechanism.

To determine if acetic or formic acid were necessary, an attempt was made to prepare the sulfone **2a** in molten ammonium formate. No sulfone was formed. We take this as indicative of the fact that the ammonium ion cannot serve as the acid. In an attempt to substitute another hydride donor for formate ion, a run was carried out in methanol–sodium borohydride. Again no sulfone resulted. Together, these facts may imply that reduction of sulfur dioxide to sulfoxylic acid (**5**) requires protonation prior to reduction.



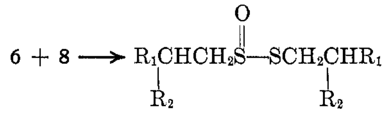
$$6 \xrightarrow{[H]} [R_1\underset{R_2}{C}HCH_2SOH] \xrightarrow{[H]} R_1\underset{R_2}{C}HCH_2SH$$

**7**

**8a**, $R_1 = H$; $R_2 = CONH_2$
**b**, $R_1 = H$; $R_2 = COOH$

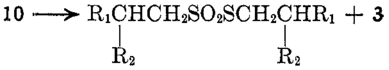
$$7 + 8 \longrightarrow 3 + H_2O$$

The formation of disulfide **3** in these reactions may be explained on the basis of intermediate sulfinic acid **6**. In reducing media sulfinic acids are known to produce disulfides, presumably *via* reduction to the sulfenic acid **7** and thence to mercaptan **8**.[11] Condensation of these two species would then yield disulfide **3**. Also mercaptan **8** and sulfinic acid **6** could condense to form a thiosulfinate **10**. The latter are known to undergo acid-catalyzed disproportionation to thiosulfonates **11** and disulfides **3**.[12] In addition, thiosulfonates (**11**) and mercaptans (**8**) are known to yield disulfides (**3**) along with sulfinic acids (**6**).[13]



$$6 + 8 \longrightarrow R_1\underset{R_2}{C}HCH_2\overset{O}{\overset{\|}{S}}{-}SCH_2\underset{R_2}{C}HR_1$$

**10**



$$10 \longrightarrow R_1\underset{R_2}{C}HCH_2SO_2SCH_2\underset{R_2}{C}HR_1 + 3$$

**11**

$$11 + 8 \longrightarrow 3 + 6$$

Mercaptan **8** could also arise from solfoxylic acid **5**. It is known that the latter disproportionates to sulfur dioxide, water, and hydrogen sulfide.[14] Addition of the latter to olefin **1** could then yield mercaptan **8**.

In the presence of base, aliphatic mercaptans are known to react with elemental sulfur to form disulfides **3** when the ratio of mercaptan to sulfur is greater than 2 mol/g-atom.[15] Hydrogen sulfide is the by-product and it could react with more olefin **1** to generate more mercaptan **8**.

$$8 + S^0 \longrightarrow 3 + H_2S$$
$$1 + H_2S \longrightarrow 8$$

In order to test the validity of these possibilities the following experiments were performed.

(1) Sodium benzenesulfinate was treated with acetic acid–ammonium formate. Though a small amount of odorous solid material was isolated it was not identified. It was probably diphenyl disulfide. The presence of thiophenol (the expected by-product) was noted by tlc. Thus, since aliphatic sulfinic acids are less stable than the aromatics,[10] the formation of disulfide **3** *via* sulfinic acid **6** seems possible.

(2) Reaction of 3-mercaptopropionic acid (**8b**) with sodium benzenesulfinate under normal reaction conditions led to the isolation of disulfide **3b** in low yield. This could arise from the presumed intermediate disulfide **12** by thiol exchange. Under the same conditions 3-mercaptopropionic acid (**8b**) alone did not yield disulfide **3b**. This result would support disulfide formation *via* thiosulfinates (**10**), especially since the aliphatic sulfinic acids would be expected to be more reactive (acidic) than the benzenesulfinic acids[10] used in this test.

$C_6H_5SSCH_2CH_2COOH$
**12**

(3) Reaction of 3-mercaptopropionic acid (**8b**) with elemental sulfur in acetic acid–ammonium formate led to an 86% yield of disulfide **3b**. Thus reaction of mercaptan with elemental sulfur seems the most likely route to disulfide.

It is possible that elemental sulfur arises from sulfoxylic acid (**5**). It has been reported that its disproportionation products in acidic solution include sulfur dioxide and sulfur.[16] By repetition of the cycle sulfur dioxide could be completely converted to sulfur. Indeed we have demonstrated that formate ion does bring about this reduction.

In an attempt to observe any previously undetected products, a pmr spectrum of a crude reaction mixture from acrylamide (**1a**) was examined. Some propionamide was observed along with sulfone **2a** and unreacted olefin **1a** in about an 8:46:46 ratio. The propionamide probably arises by reduction of acrylamide, which is an eneamide.[2] About 1 mol of formate ion/mol of sulfur dioxide added was consumed as previously reported.[1a] No other products could be detected, although the presence of the methyl resonance of acetic acid could obscure the –SH of any mercaptan (**8a**) present. In most of the reaction mixtures a foul mercaptan-like odor was noted.

It appears that all the findings can be reasonably rationalized on the basis of these proposals. Formation of disulfide **3a** by use of twice the normal amount of solvent formic acid–trimethylamine (3.0:1.0) is probably a reflection of the instability of sulfoxylic acid and sulfinic acid **6a**. Since their concentrations as well as that of the olefin were halved, the rate of sulfone formation decreased (by a factor of eight assuming bimolecular reactions) to the point where disproportionation of these species successfully competed. Acetic acid–ammonium formate is not so effective for the disproportionations, since under comparable conditions it

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[11] J. Strating and H. Backer, *Recl. Trav. Chim. Pays-Bas*, **69**, 638 (1950).

[12] C. G. Venier, Ph.D. Thesis, Oregon State University, 1967; *Diss. Abstr. B*, **28**, 3873 (1967).

[13] T. F. Lavine, *J. Biol. Chem.*, **113**, 571, 583 (1936); L. Field, *J. Amer. Chem. Soc.*, **83**, 4414 (1961).

[14] E. Marshak, *Khim. Nauka Prom.*, **2**, 524 (1957); *Chem. Abstr.*, **52**, 6040c (1958).

[15] B. D. Vineyard, *J. Org. Chem.*, **32**, 3833 (1967).

[16] H. Stamm and M. Goehring, *Angew. Chem.*, **58**, 52 (1945).

does not lead to disulfide. In view of the relative acidities of the two acids this is the expected trend.[12,17] The difference may, in part, be due to the reservoir of excess formate ion in the formic acid system, which could allow more efficient conversion of sulfur dioxide to sulfur and hence to disulfide as outlined above. In addition other sulfinic acids (**6**) apparently are not so sensitive to disproportionation since a similar solvent effect was not evident in other systems. Use of acetic acid is preferred for bringing about sulfone formation in general.

Based on the mechanism one might expect that unsymmetrical sulfones would result from reaction of two olefins, one which is capable of adding sulfoxylic acid and one which is not. Acrylamide and methyl methacrylate presumably undergo sulfinic acid formation as evidenced by isolation of the corresponding sulfone and disulfide, respectively (see Table I). Styrene and linear olefins (as exemplified by 1-decene) apparently do not give rise to a sulfinic acid since no disulfides or sulfones were detected. Crossed reactions were thus attempted between acrylamide:styrene and methyl methacrylate:1-octene; no unsymmetrical product was isolated in either instance. Apparently, ability to undergo addition of sulfoxylic acid is a necessary but not sufficient condition for addition of sulfinic acid.

The structural requirements for the olefin (**1**) appear to be a combination of electronic and steric effects (as is usually the case). First, it appears that powerful electron-withdrawing groups are required for both eq 2 and 3. This is known for condensations of sulfinate salts with olefins.[9] Probably both of these steps involve attack of the conjugate bases on the olefin with formation of a carbanion. Second, both steps exhibit a steric effect. Although fumaric acid satisfies the electronic requirements for sulfinic acid formation, this did not occur, *i.e.*, no disulfide, mercaptan, or sulfone were isolated; and, while methyl methacrylate (**1e**) forms the corresponding sulfinic acid (as shown by isolation of disulfide), reaction of the latter with olefin does not occur. In a crossed reaction of methyl methacrylate (**1e**) and acrylamide (**1a**), none of the unsymmetrical sulfone was isolated. This indicates that the presence of a methyl group on the olefin causes sufficient steric hindrance that no attack occurs, since sulfinic acid **6a** would be more reactive than sulfinic acid **6b** derived from methyl methacrylate owing to its lower steric bulk. That the latter is true is shown by the fact that the methyl methacrylate derived sulfinic acid **6b** did not react with acrylamide (**1a**).

The high yield of disulfone **4** is probably the result of the highly favorable entropy situation in the sulfinic acid derived from divinyl sulfone (**1**, $R_1 = H$; $R_2 = SO_2CH{=}CH_2$). Thus, reaction of the sulfinyl group with the adjacent double bond occurs before side reactions can take place.

## Experimental Section

**General.**—Infrared spectra were recorded on a Beckman IR-5, solids in KBr, liquids neat. Pmr spectra were recorded on a Varian A-60A instrument. Chemicals shifts are relative to TMS ($\delta$ 0.00). The mass spectra were recorded on a Varian M-66 cycloidal focusing instrument. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich. Samples were routinely examined by thin layer chromatography on Eastman silica gel sheets using a benzene–methanol–acetic acid (82:9:9) solvent system and iodine as developer. Melting points were taken in capillaries on a Thomas–Hoover apparatus and are uncorrected. Boiling points are likewise uncorrected. The disulfide **3d** from methyl methacrylate was examined on a Perkin-Elmer 154B vapor fractometer using a 6 ft × 0.25 in. 5% Carbowax 20M on Chromosorb W column at 170° and a flow rate of 55 ml/min. Two peaks of retention times 13 and 24 min and of about 1.0:1.5 area ratio were observed.

**Materials.**—The formic acid used in this work was from Aldrich (97+%) and Matheson (98–100%). The sulfur dioxide was Matheson anhydrous grade, 99.98% pure. All the olefins were commercial samples and were used without further purification. Other materials were also employed as received.

**Formic Acid–Tertiary Amine Azeotropes.**—To 57.5 ml (1.48 mol) of formic acid was added 33.6 g (0.569 mol) of gaseous trimethylamine with cooling. Distillation through a 3-in. Bantamware Vigreux column gave a center cut of constant bp 115.5° (62 mm); pmr (neat) $\delta$ 2.90 (s, 4.4 H, $N(CH_3)_3$), 8.3 (s, 1.0 H, HCOOH), 13.1 (s, 1.0 H, HCOOH). Examination by vpc (6 ft × 0.25 in. Poropak S column at 160° and 60 ml/min flow) and infrared indicated the presence of no new compounds. Redistillation gave a center cut of constant bp 39–40° (0.80 mm): pmr (neat) $\delta$ 2.90 (s, 3.5 H, $N(CH_3)_3$), 8.3 (s, 1.0 H, HCOOH), 13.1 (s, 1.0 H, HCOOH). Ratio of HCOOH:$N(CH_3)_3$ = 2.0:1 (62 mm), 2.6:1 (0.80 mm).

A mixture of 29.8 g (0.645 mol) of formic acid and 39.9 g (0.215 mol) of tributylamine was distilled through a 3-in. Bantamware Vigreux column to afford a center cut of constant bp 70° (0.92 mm); pmr (neat) $\delta$ 1.2–3.2 (m, 14 H, $N[(CH_2)_3CH_3]_3$), 8.50 (s, 1.0 H, HCOOH), 13.80 (s, 1.0 H, HCOOH). Redistillation gave a center cut of constant bp 134° (55 mm); pmr (neat) $\delta$ 1.2–3.2 (m, 12 H, $N[(CH_2)_3CH_3]_3$), 8.50 (s, 1.0 H, HCOOH), 13.6 (s, 1.0 H, HCOOH). Vpc (as above) and infrared examination indicated the presence of no new covalent compounds. Ratio of HCOOH:$N[(CH_2)_3CH_3]_3$ = 2.0:1.0 (0.92 mm), 2.3:1.0 (55 mm).

**General Procedure for Reaction of Olefins and Sulfur Dioxide.**—To a rapidly stirred solution of 0.100 mol of the olefin and 0.05 g of phenothiazine (to inhibit polymerization) in the desired solvent system maintained at 100 ± 2° under a reflux condenser was added 0.0500 mol of sulfur dioxide on a stream of nitrogen over a period of 1 hr (3 hr where noted). The sulfur dioxide was condensed in a graduated tube and measured by volume (2.24 ± 0.01 ml) based on a density of 1.43 g/ml at its boiling point (−10°).[18] The nitrogen purging was continued for 0.25 hr and the mixture was poured onto ice and filtered. The solid was washed with water and dried to yield the sulfone, disulfide, or sulfur. The filtrate was concentrated and extracted with ether. After washing with sodium bicarbonate and water, the extract was dried ($MgSO_4$ or $Na_2SO_4$) and the solvent was removed to afford the disulfide in cases where it was liquid. (See Table VII.)

TABLE VII

SPECIFIC CONDITIONS

| Condition | Solvent system (molar ratios) | Weight used, g |
|---|---|---|
| A | HCOOH (3.0)–$NMe_3$ (1.0) | 19.8 |
| B | HCOOH (3.0)–$NMe_3$ (1.0) | 39.6 |
| C | $CH_3COOH$ (1.7)–$NH_4OOCH$ (1.0) | 34.6 |
| D | HCOOH (1.2)–$NH_4OOCH$ (1.0) | 25.6 |
| E | HCOOH (3.0)–$NMe_3$ (1.0) | 9.9 |

**Phenyl 2-Carboxamidoethyl Sulfone** (**9**).—A solution of 8.21 g (0.0500 mol) of sodium benzenesulfinate, 3.55 g (0.0500 mol) of acrylamide, 0.05 g of phenothiazine, 13.6 g (0.216 mol) of ammonium formate, and 21.0 ml (0.366 mol) of acetic acid was heated at 100° under nitrogen for 1.25 hr. The mixture was poured onto ice and filtered to yield a total of 9.55 g (90%) of colorless needles: mp 127.0–127.5° (lit.[19] mp 126–127°); pmr (25% w/w $CF_3COOH$) $\delta$ 2.99 (2 H, t, $J = 6$ Hz), 3.75 (12 H, t, $J = 6$ Hz), 7.8 (6 H, m).

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[17] P. Allen, Jr. and L. Reich, *J. Phys. Chem.*, **64**, 1928 (1960); J. Kice and K. Bowers, *J. Amer. Chem. Soc.*, **84**, 605 (1962).

[18] See reference in footnote *i* of Table I.

[19] O. Achmatowicz and J. Michalski, *Rocz. Chem.*, **30**, 243 (1956).

**Basic Cleavage of Phenyl 2-Carboxamidoethyl Sulfone (9).**—This was carried out by the general method of Bradley[20] using 5.30 g (0.136 mol) of sodamide, 35 ml of piperdine, and 6.60 g (0.0310 mol) of the sulfone. It yielded 10.7 g of nearly colorless powder. This material was shown to contain sodium hydroxide by titration with acid. From the integral ratios of the aliphatic to aromatic signals the ratio of sodium 2-carboxamidoethyl sulfinate to sodium benzenesulfinate was calculated to be about 2:1.

**Reaction of Sodium 2-Carboxamidoethyl Sulfinate (6a) and Acrylamide (1a).**—A solution of 4.0 g of the mixture of salts (**6a** and **1a**), 1.0 g of acrylamide, and 10 ml of formic acid was refluxed 1 hr and poured onto ice. Filtration yielded 0.60 g of stout needles, part melted at 115°, rest at 205–210°. Tlc of the solid showed spots of $R_f$ 0.00 and 0.23. Bis(2-carboxamidoethyl) sulfone and phenyl 2-carboxamidoethyl sulfone have $R_f$ of 0.00 and 0.23, respectively.

**Exchangeability of Bis(2-carboxamidoethyl) Sulfone (2a). 1. In Sodium Formate–Acetic Acid–Deuterium Oxide.**—A mixture of 3.50 g (0.0168 mol) of the sulfone, 7.35 g (0.108 mol) of ammonium formate, 11.5 ml (0.636 mol) of deuterium oxide, and 21.0 ml (0.368 mol) of acetic acid was heated at 100° under nitrogen for 1.25 hr. The mixture was cooled and filtered. The solid was washed with ether and dried to yield 3.54 g of colorless solid, mp 215–218°. A blank solution of 0.2500 g (0.001200 mol) of starting material, 0.0580 g (0.0005680 mol) of pivalic acid, and 0.75 ml of trifluoroacetic acid was examined by pmr. Ratio of $CH_2:CH_2$ (sulfone):$CH_3$ (pivalic acid) found was 1.00:1.00:1.07; theoretical for no exchange 1.00:1.00:1.03. A solution of 0.2501 g (0.001201 mol) of the product and 0.0593 g (0.0005808 mol) of pivalic acid in trifluoroacetic acid showed a ratio of 1.00:1.00:1.04 *vs.* the theoretical for no exchange 1.00:1.00:1.09.

**2. In Trifluoroacetic Acid-*d*.**—A solution of 0.1297 g (0.0006227 mol) of the sulfone and 0.0224 g (0.0002194 mol) of pivalic acid in 0.6 g of trifluoroacetic acid-*d* was warmed a few minutes, allowed to stand 24 hr, and examined by pmr. The $CH_2:CH_2:CH_3$ ratio was found to be 1.38:1.38:1.00 (theoretical for no exchange 1.31:1.31:1.00).

**3. Under Reaction Conditions.**—A mixture of 1.00 g (0.00481 mol) of the sulfone, 2.10 g (0.00309 mol) of sodium formate, and 6.0 ml (0.10 mol) of acetic acid-$d_4$ was heated at 100° for 2 hr and then cooled and filtered. The solid was washed with water and ether. Pmr analysis of a solution of 0.1018 g (0.0004887 mol) of the sulfone, 0.0120 g (0.0001175 mol) of pivalic acid, and 0.6 g of trifluoroacetic acid showed a $CH_2:CH_2:CH_3$ ratio of 1.83:1.83:1.00 (theoretical for no exchange 1.84:1.84:1.00).

**Preparation of Bis(2-carboxamidoethyl) Sulfone (2a) in Sodium Formate-*d* and Acetic Acid-$d_4$.**—To a solution of 1.21 g (0.0170 mol) of acrylamide, 1.25 g (0.0184 mol) of sodium formate-*d*, 0.01 g of phenothiazine, and 2.50 ml (0.0438 mol) of acetic acid-$d_4$ was added 0.38 ml (0.0085 mol) of sulfur dioxide in the usual manner over a 1-hr period. The mixture was cooled, filtered, washed with 10 ml of water and ether, and dried to afford 0.55 g (31%) of colorless solid, mp 216–218° dec. The pmr spectrum of a 25% solution in trifluoroacetic acid showed broad singlets at $\delta$ 3.8 and 3.2 in a 1.15:1.00 ratio.

**Preparation of Bis(2-carboxamidoethyl) Sulfone (2a) Using Sodium Formate-*d*. Run A.**—To a solution of 2.42 g (0.0341 mol) of acrylamide, 0.05 g of phenothiazine, 2.50 g (0.0367 mol) of sodium formate-*d*, and 7.0 ml (0.122 mol) of acetic acid at 100° was added 0.76 ml (0.0170 mol) of sulfur dioxide on a stream of nitrogen over a period of 1 hr. After stirring 0.25 hr, the mixture was poured onto ice to give 1.85 g (52%) of solid. Ether washing and recrystallization gave colorless needles, mp 228.5–229.0°. Pmr integrations of the signals at $\delta$ 3.8 and 3.2 gave an average (three runs) ratio of 0.96:1.00, respectively.

**Run B.**—This was carried out as run A but using only one-half the amount of acetic acid (3.50 ml, 0.061 mol). Pmr analyses yielded an average integral ratio of 0.90:1.00 for the signals at $\delta$ 3.8 and 3.2.

**Statistical Calculation of Integral Ratios ($\alpha:\beta$).**—Assuming complete exchange of the acidic protons of acetic acid and the NH protons of the amide groups, the initial percentage of deuterium present was calculated. The final proportion of deuterium was calculated differently for the various possible mechanisms. For the termolecular mechanism with no exchange of protons in the intermediate sulfinic acid, the final number of protons and deuterons was the same as the initial. For the termolecular mechanism with exchange of the protons $\alpha$ to the sulfinyl group in the sulfinic acid the final total number of protons is equal to the initial number plus the number of moles of formate ion theoretically utilized. For the three-step mechanism with exchange of the intermediate sulfinic acid, the final number of protons and deuterons is equal to the initial number plus the number of moles of formate ion theoretically utilized. For the three-step mechanism with exchange of the acidic proton and the protons $\alpha$ to the sulfinic acid group in the intermediate sulfinic acid, the final number of protons and deuterons is equal to the initial number plus the number of moles of formate ion theoretically used and twice the number of moles of sulfinic acid generated. The initial and final percentages of protium were averaged for calculation of the area ratios.

**Reaction of Acrylamide (1a) and Sulfur Dioxide in Molten Ammonium Formate.**—To a solution of 20.5 g (0.324 mol) of ammonium formate, 7.10 g (0.100 mol) of acrylamide, and 0.05 g of phenothiazine at 135° was added 2.24 ml (0.050 mol) of sulfur dioxide over 1 hr. No solid precipitated when the mixture was poured onto ice. The mixture was taken to dryness and extracted with hot methanol to yield about 10 g of a solid–liquid mixture. Tlc showed spots of $R_f$ 0.06 and 0.81. $R_f$'s of knowns are as follows: ammonium formate, 0.06; acrylamide, 0.46; propionamide, 0.32; bis(2-carboxamidoethyl) sulfone, 0.00; bis(2-carboxamidoethyl) disulfide, 0.37. The spot of $R_f$ 0.81 was not identified.

**Reaction of Acrylamide (1a), Sulfur Dioxide, and Sodium Borohydride in Methanol.**—To a solution of 6.35 g (0.0894 mol) of acrylamide, 0.85 g (0.022 mol) of sodium borohydride, 0.05 g of phenothiazine, and 25 ml of methanol at 50° was added 2.0 ml (0.0046 mol) of sulfur dioxide over a period of 1 hr. No solid formed when the mixture was poured onto ice. The odor of sulfur dioxide was noted.

**Reaction of Sodium Benzenesulfinate with Ammonium Formate–Acetic Acid.**—A solution of 8.21 g (0.0500 mol) of sodium benzenesulfinate, 0.05 g of phenothiazine, 13.6 g (0.216 mol) of ammonium formate, and 21.0 ml (0.366 mol) of acetic acid was heated at 100° for 1.25 hr under nitrogen. When poured onto ice the mixture yielded no solid. The mixture contained thiophenol as shown by tlc. It was taken to dryness *in vacuo* and extracted with benzene to yield a small amount (~0.05 g) of solid with the odor of burning rubber. The residue was redissolved in water and treated with a saturated solution of ferric chloride to precipitate 4.3 g of the ferric salt of sulfinic acid. In a blank 8.21 g of sodium benzenesulfinate yielded 7.3 g (91%) of the salt.

**Reaction of Sodium Benzenesulfinate with 3-Mercaptopropionic Acid (8b).**—A solution of 4.25 ml (0.0500 mol) of 3-mercaptopropionic acid, 8.21 g (0.0500 mol) of sodium benzenesulfinate, 13.7 g (0.216 mol) of ammonium formate, and 21 ml (0.366 mol) of acetic acid was heated at 100° for 1.25 hr and then poured onto ice. The aqueous mixture was extracted with ether and washed with water. The aqueous portion on evaporation yielded 1 g (19%) of dithiodipropionic acid (**3b**), mp 151–154°, undepressed with an authentic sample. The ether portion yielded 0.2 g of a malodorous oil. Tlc showed the presence of thiophenol and another component. It was not examined further. A blank run without sodium benzenesulfinate yielded no disulfide.

**Reaction of 3-Mercaptopropionic Acid (8b) and Sulfur.**—To a stirred solution of 1.20 g (0.0375 g-atom) of sulfur, 6.81 g (0.108 mol) of ammonium formate, and 10.5 ml (0.183 mol) of acetic acid over a 50-min period was added 12.5 g (0.188 mol) of 3-mercaptopropionic acid. After stirring 25 min, the mixture was allowed to cool and then filtered. The odor of hydrogen sulfide was noted. There was obtained 10.6 g (86%) of colorless solid, mp 155–156° after one recrystallization from water. The pmr spectrum was identical with that of an authentic sample of **3b**.

**Reaction of Sulfur Dioxide with Ammonium Formate–Acetic Acid.**—To a solution of 13.6 g (0.216 mol) of ammonium formate and 21.0 ml (0.366 mol) of acetic acid at 100° was added 1.80 ml (0.0403 mol) of sulfur dioxide in the usual manner over 1.5 hr. The yellow suspension was then poured into water and filtered to yield 0.4 g (31%) of elemental sulfur, mp 120–121°, which burned with a blue flame to produce sulfur dioxide (lit.[21] mp 120° for amorphous sulfur).

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[20] W. Bradley, *J. Chem. Soc.*, 458 (1938).

[21] Reference 5, p 664.

**Pmr Analysis of Crude Mixture From Acrylamide Reaction.**—The reaction was run in the usual manner using 3.55 g (0.050 mol) of acrylamide, 6.81 g (0.108 mol) of ammonium formate, 10.5 ml of acetic acid, and 1.12 ml (0.0250 mol) of sulfur dioxide. The pmr spectrum (in CF$_3$COOH) showed signals due to acrylamide (m, $\delta$ 6.2 and 6.5), the sulfone (t, $\delta$ 3.1 and 3.7), and propionamide (s, $J = 7.5$ Hz, $\delta$ 1.3). The area ratio was about 6:6:1, respectively. No mercaptan was detected, though it could have been obscured by the methyl signal (s, $\delta$ 2.2) of acetic acid.

**Registry No.**—**2a,** 13063-92-8; **2b,** 6291-88-9; **2c,** 3234-31-9; **2d,** 5450-67-9; **3a,** 1002-19-3; **3b,** 1119-62-6; **3c,** 15441-06-2; **3d,** 25055-41-8.

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# Sulfonium Salts. IV. Cleavage-$\alpha$-Substitution Competition of Dibenzylhalosulfonium Salts

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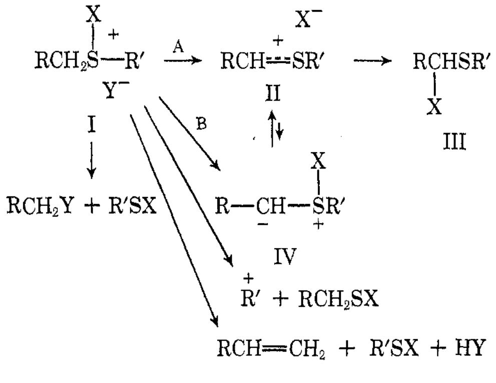
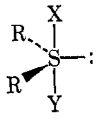
Benzyl sulfide reacts with chlorine, bromine, NCS, and NBS to provide $\alpha$-halobenzyl benzyl sulfide, benzyl halide, benzylsulfenyl halide, and, where possible, N-benzylsulfenylsuccinimide. The competitive isotope effects, measured in deuteriochloroform and carbon tetrachloride, are consistent with an E2-type elimination from an initially formed halosulfonium salt. The variation of the ratio of cleavage to $\alpha$-halogenated products is consistent with a rate-determining step involving halide ion attack on a single intermediate when initial concentrations of halogen and sulfide are low, but involving decomposition of aggregates when initial concentrations above about 0.3 *M* are used.

Bromination and chlorination of sulfides bearing an $\alpha$ proton at low temperatures in nonpolar aprotic solvents often leads to the formation of metastable adducts[2] (I) which usually decompose upon warming to give $\alpha$-halo sulfides[3] (III) (Scheme I). Reactions of sulfides with chlorine,[3–5] sulfuryl chloride,[5–7] and N-halosuccinimides[8] to produce $\alpha$-halo sulfides are all considered to proceed through adduct I, generally considered to be a halosulfonium salt.

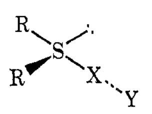
SCHEME I



The largest contributor to the structure of the sulfide–bromine adduct would seem to be ionic on the basis of X-ray,[9] nmr,[9] and conductometric[2d] data. Contributions to the time-averaged structure in solution by the trigonal bipyramidal dihalosulfurane V in analogy with the crystal structure of the adduct of chlorine with bis($p$-chlorophenyl) sulfide[10] or the charge transfer type structure[11] VI are not excluded by available data. In fact, the X-ray data[9] is compatible with a much distorted charge transfer structure.



V



VI

In lieu of reorganizing to $\alpha$-halo sulfides and HX, possibly by way of ylide IV and sulfocarbonium ion II, halosulfonium salts can undergo carbon–sulfur bond rupture to provide sulfenyl halides and alkyl halides directly either by displacement on carbon[12] or by way of stable carbonium ions.[13] Reactions involving carbon–sulfur fragmentations of halosulfonium salts have also been observed.[14]

## Results

The reactions of benzyl sulfide with several halogenating agents such as N-chlorosuccinimide (NCS),

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[1] Submitted by M. G. Huang in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

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