Reaction of Dimethyl Tetrasulfide with Unsaturated Compounds

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The reactions of dimethyl tetrasulfide with unsaturated compounds were investigated. Dimethyl tetrasulfide is known to dissociate homolytically on heating and disproportionates into a mixture of polysulfides. The initiated polymerization of methyl methacrylate is accelerated by addition of a very small amount (*ca.* 10^{-5} to 10^{-4} mole/l.) of dimethyl tetrasulfide, but, when the concentration of the tetrasulfide is increased, retardation of the rate of polymerization occurs. Dimethyl tetrasulfide initiates polymerization of acrylonitrile, but on increasing the concentration of the tetrasulfide degradative chain transfer is again observed. Diethyl maleate isomerizes into the fumarate in the presence of dimethyl tetrasulfide. The slow saturation of double bonds in unsaturated compounds is observed in the presence of an equimolar amount of dimethyl tetrasulfide at 130°. Products of the reaction showed that the saturation of double bonds resulted mainly from the interaction with methylthiyl radicals and the Markovnikov-type addition is apparently predominant. A plausible explanation of the formation of the Markovnikov-type product by free-radical mechanism is discussed.

The mechanism of reactions between dialkyl tetrasulfides and unsaturated compounds has considerable importance in polysulfide chemistry. It is reported in the literature that the tetrasulfide decomposes into disulfide or thiol and elemental sulfur and produces Markovnikov addition products with olefin.[4-6] In the reaction system sulfur acts as an inhibitor for the free-radical reaction and the mechanism of reaction is proposed as ionic.

Recently Tobolsky, *et al.*,[7] confirmed that the thermal decomposition of dimethyl tetrasulfide produced radicals probably of the $RS_2 \cdot$ type. The rate of radical production was measured by a stable free-radical technique. The bond dissociation energy of the S–S bond in dimethyl tetrasulfide was calculated as 36 kcals/mole, which is close to that of the elemental sulfur.

This paper deals with the mechanism of reactions between the free radicals which were generated by the thermal decomposition of dimethyl tetrasulfide and several unsaturated compounds. The free radicals were allowed to react with the double bond, resulting in the initiation of vinyl polymerization, *cis–trans* isomerization, and the formation of addition products. The rate of these reactions was followed by nmr, gas–liquid partition chromatography (glpc), and polymer formation measurements.

Results and Discussion

Disproportionation of Dimethyl Tetrasulfide.—At 80° dimethyl tetrasulfide decomposed and disproportionated into a mixture of dimethyl tri-, tetra-, penta-, hexa-, and probably higher polysulfides as measured by nmr. No dimethyl monosulfide was detected, and a small amount of the disulfide appeared only after prolonged heating (Table I). At an elevated temperature (130°), an apparent two-stage equilibrium process has been observed (Table II). The first equilibrium was established very rapidly, within 1 hr, and showed

TABLE I

DISPROPORTIONATION OF DIMETHYL TETRASULFIDE[a] AT 80°

Time, hr	$(CH_3)_2S_2$	$(CH_3)_2S_3$	Mole % $(CH_3)_2S_4$	$(CH_3)_2S_5$	$(CH_3)_2S_6$
0	...	4.4	95.6	...	...
2.5	...	22.0	58.0	16.0	4.0
5.2	...	31.0	48.2	15.5	5.2
10.1	...	40.8	38.0	14.8	6.3
20.2	...	46.0	39.3	12.3	2.5
43.8	...	46.7	30.7	15.3	7.3
65.6	...	45.7	28.3	17.4	8.7
109.9	...	44.6	30.8	18.5	6.2
237.2	3.5	42.3	28.5	16.6	9.2

[a] As measured by nmr.

TABLE II

DISPROPORTIONATION OF DIMETHYL TETRASULFIDE AT 130°

Time, hr	$(CH_3)_2S_2$	$(CH_3)_2S_3$	Mole % $(CH_3)_2S_4$	$(CH_3)_2S_5$	$(CH_3)_2S_6$	Total S, calcd
0	...	7.0	93.0	...	...	100
1	...	47.5	27.5	15.6	10.6	100
4	0.8	45.5	26.4	14.8	12.8	100
8.9	3.7	42.5	24.6	18.6	10.4	99.0
16.5	8.9	41.0	25.6	12.1	11.6	95.0
28.5	11.7	37.8	25.1	13.5	11.7	95.3
53.5	16.7	34.5	24.4	13.4	11.2	93.8
77.5	18.4	31.0	24.3	12.9	13.7	95.1
117.8	19.0	30.7	24.7	12.8	12.8	94.1

the appearance of dimethyl tri-, penta-, hexa-, and probably higher polysulfides. The dimethyl disulfide appeared to form gradually after the first equilibrium, and a new equilibrium was reestablished among dimethyl di-, tri-, tetra-, penta-, hexa-, and polysulfides. The latter process required about 100 hr.

The first process is assumed to be the initial decomposition of dimethyl tetrasulfide into methylthiothiyl radical $(CH_3S_2 \cdot)$ and the subsequent disproportionation occurs by the interaction of that radical with the sulfide. The slow formation of dimethyl disulfide during the latter process may be interpreted as a result of slower rate of production of methylthiyl radical $(CH_3S \cdot)$ in the reaction mixture.

Since dimethyl trisulfide decreased quite markedly during the latter process, it might play an important role here. According to Trivette and Coran,[8] diethyl trisulfide and dipropyl trisulfide gave an exchanged trisulfide at 130–150°. Hence dimethyl trisulfide, may be able to exchange for itself at 130°, and it may be related to the slow formation of $CH_3S \cdot$ radical and to the slow production of dimethyl disulfide. The total

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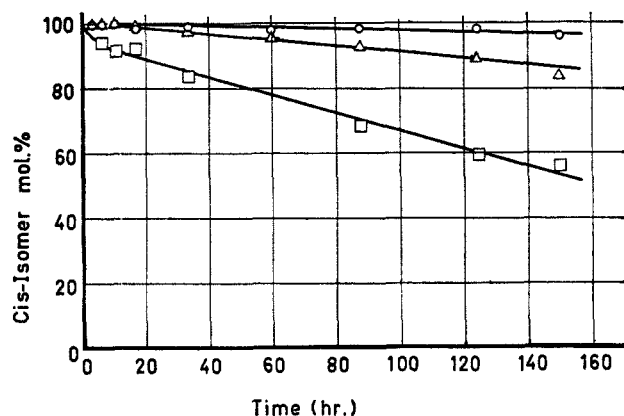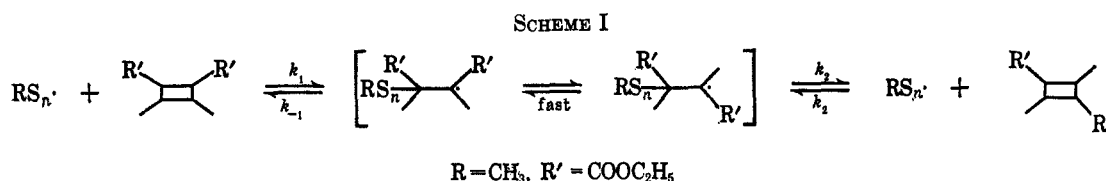
(8) C. D. Trivette, Jr., and A. Y. Coran, *J. Org. Chem.*, **31**, 100 (1965).

SCHEME I

$$RS_n\cdot \ + \ \underset{R'}{\overset{R'}{\diagdown}}\diagup \ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \ \left[RS_n\diagdown\diagup \ \underset{fast}{\rightleftharpoons} \ RS_n\diagdown\diagup_{R'}\right] \ \underset{k_2}{\overset{k_2}{\rightleftharpoons}} \ RS_n\cdot \ + \ \underset{R'}{\overset{R'}{\diagdown}}\diagup_{R'}$$

$$R = CH_3, \ R' = COOC_2H_5$$

Figure 1.—Isomerization of diethyl maleate at 80°: ◯, neat; △, $(CH_3)_2S_3$; ☐, $(CH_3)_2S_4$.
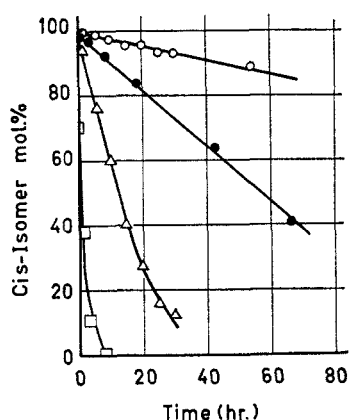
Figure 2.—Isomerization of diethyl maleate at 130°: ◯, neat; ●, $(CH_3)_2S_2$; △, $(CH_3)_2S_3$; ☐, $(CH_3)_2S_4$.

amount of sulfur in the dimethyl sulfides, determined by material balance calculation, is also shown in Table II. Despite the old belief, within the experimental error, no elemental sulfur formation is conceivable.

cis-trans **Isomerization of Diethyl Maleate.**—The isomerization of diethyl maleate was studied at 80 and 130° in the presence of dimethyl di-, tri-, and tetrasulfide (Figures 1 and 2). The interesting feature in the isomerization studies is that in the presence of dimethyl tetrasulfide at 130° the complete isomerization (*cis* to *trans*) occurs within the period of the first equilibrium distribution of the decomposition of dimethyl tetrasulfide. Therefore, the isomerization in this case is assumed to be catalyzed, essentially by $CH_3S_2\cdot$ type.

Also, at 80° the decomposition of dimethyl tetrasulfide yields mainly $CH_3S_2\cdot$; hence it is more likely that the isomerization was catalyzed again by $CH_3S_2\cdot$ type. During the period of isomerization, only a negligible amount of double bond was saturated. The reaction can be represented as shown in Scheme I.

Initiated Polymerization of Methyl Methacrylate in the Presence of Dimethyl Tetrasulfide.—Methyl methacrylate was polymerized with azobisisobutylonitrile in

the presence of dimethyl tetrasulfide at 58.9 ± 0.1°. At higher concentration of dimethyl tetrasulfide, polymerization of methyl methacrylate is retarded appreciably; however, when the amount of dimethyl tetrasulfide is reduced, the rate of polymerization seems to increase and finally exceeds that without dimethyl tetrasulfide. This observation indicates the possiblity of initiation by dimethyl tetrasulfide (Table III).

TABLE III

ACCELERATION AND RETARDATION OF POLYMERIZATION OF METHYL METHACRYLATE BY DIMETHYL TETRASULFIDE[a]

[Dimethyl tetrasulfide] $\times$ 10⁴ moles/l.	$\Delta M/\Delta t \times 10^4$ moles/l. sec	Rel rates
0	3.42	1.00
0.25	4.42	1.33
0.50	3.82	1.15
0.75	3.75	1.13
3.00	3.50	1.02
5.00	3.49	1.02
7.00	2.78	0.813
9.55	2.61	0.761
15.0	2.18	0.637
19.1	1.93	0.564
20.0	1.97	0.576
30.0	1.64	0.480
38.3	1.47	0.430
40.0	1.46	0.427

[a] Methyl methacrylate, 6.77 moles/l.; benzene, 3.90 moles/l.; azobisisobutylonitrile, 1.84×10^{-2} mole/l.; at 58.9°.

Polymerization of Acrylonitrile in the Presence of Dimethyl Tetrasulfide.—The thermal polymerization of acrylonitrile monomer is not evident.[9] On addition of a small amount of dimethyl tetrasulfide at 80 ± 0.1°, acrylonitrile polymerized and the polymer began to precipitate. The polymer conversion *vs.* reaction time plots show straight lines. In heterogeneous polymerization of acrylonitrile the rate of polymerization increases with time owing to unimolecular termination.[10] In this case, however, terminations among growing polymer radicals and the tetrasulfide or sulfenyl radicals are predominant over such an unimolecular process; Figure 3 shows a plot of $(\Delta M/\Delta t)^2$ *vs.* dimethyl tetrasulfide concentration. The plot does not show a straight line but appears to have a maximum at around 6×10^{-4} mole/l. of dimethyl tetrasulfide concentration. It is not surprising because such behavior of several initiators was reported elsewhere,[11-13] although no satisfactory explanation of this behavior is given. This fact suggests that dimethyl tetrasulfide acts not only as an initiator, but also as a degradative chain transfer agent. Figure 4 shows a linear relation-

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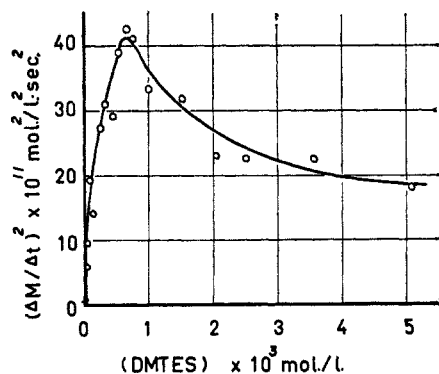(13) R. W. Haward and W. Simpson, *Trans. Faraday Soc.*, **51**, 95 (1955).

Figure 3.—Plot of the square of the rate of acrylonitrile polymerization vs. concentration of dimethyl tetrasulfide (at 80°).
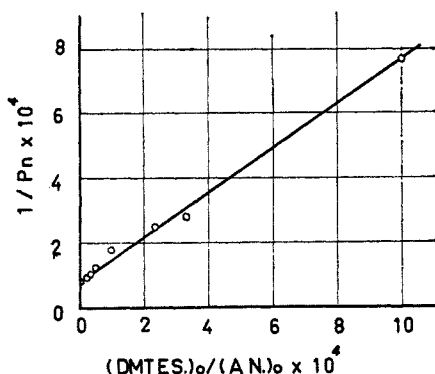

Figure 4.—$1/\bar{P}_n$ vs. [dimethyl tetrasulfide]$_0$/[acrylonitrile]$_0$. Acrylonitrile in bulk at 80°.

ship between $1/\bar{P}_n$ vs. [dimethyl tetrasulfide]$_0$/[acrylonitrile]$_0$. The apparent chain-transfer constant was calculated as $C_x = 0.69$.

The Reaction of Cyclohexene with Dimethyl Tetrasulfide.—The formation of methyl monosulfide, as shown in Figure 5, represents the product, cyclohexyl methyl monosulfide, formed by the interaction of $CH_3S\cdot$ and cyclohexene. The rate of formation of the product, expressed in terms of the fraction of the maximum amount present in the final reaction mixture, is comparable with that of the formation of dimethyl disulfide, both being directly dependent upon the concentration of $CH_3S\cdot$ radical. In Figure 5, the methyl disulfide curve represents a mixture of cyclohexyl methyl disulfide and dimethyl disulfide, which are indistinguishable by nmr alone. However, by vpc analysis the amount of cyclohexyl methyl disulfide could be determined. Table IV shows the formation

TABLE IV

CONVERSIONS INTO METHYL CYCLOHEXYL
MONO- AND DISULFIDE AT 130°

Reacn time, hr	Mole %	
	Monosulfide	Disulfide
4.8	...	...
10.5	4.5	1.2
30.0	10.0	2.7
62.5	14.5	3.3
120.	22.0	5.6

of cyclohexyl methyl mono- and disulfides during the reaction. It is evident that both products began to form simultaneously but their rates were different. An appreciably lower rate of formation of the disulfide
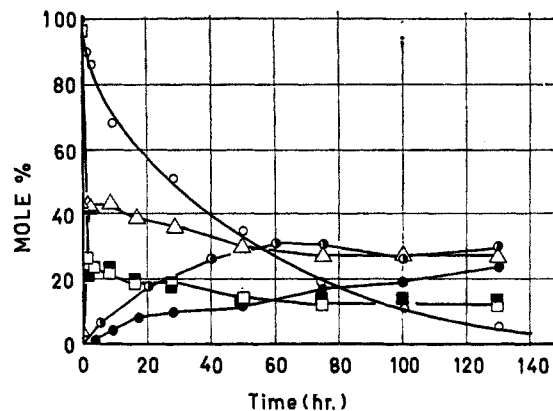

Figure 5.—Reaction of cyclohexene with dimethyl tetrasulfide at (130°): ●, $(CH_3)_2S$; ◐, $(CH_3)_2S_2$; △, $(CH_3)_2S_3$; □, $(CH_3)_2S_4$; ■, $(CH_3)_2S_5 + (CH_3)_2S_6$; ○, double bond.
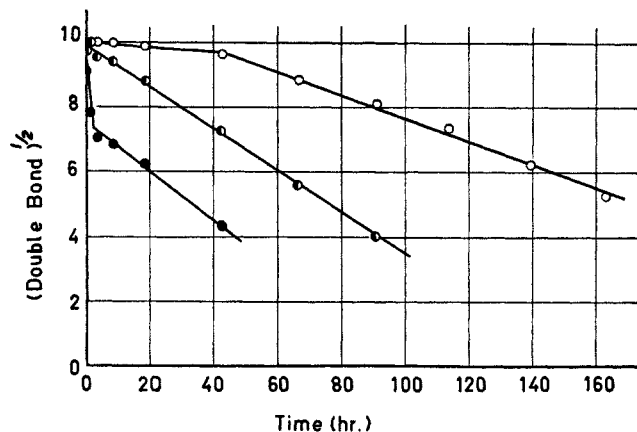

Figure 6.—One-half-order plot of the reaction of several unsaturates with dimethyl tetrasulfide: ○, diethyl maleate; ◐, 1-methylcyclohexene; ●, α-methylstyrene.

product compared with that of monosulfide, in a system where the formation of $CH_3S_2\cdot$ is much faster than the formation of $CH_3S\cdot$, is conclusive evidence for the higher addition reactivity of $CH_3S\cdot$ to the double bond of olefin.

At the first equilibrium distribution of the polysulfides, the molar concentration of dimethyl trisulfide was frequently found as twice the amount of dimethyl tetrasulfide. The cyclohexyl methyl monosulfide began to form after the attainment of the equilibrium, but, when a mixture of dimethyl tri- and tetrasulfide, in the same proportions, was taken as the initial reactant, the reaction did not proceed instantaneously as was expected. An induction period was observed and during the induction period the initial amount of dimethyl tetrasulfide disproportionated as before (1:2 proportion with trisulfide) resulting in the initial increase of dimethyl trisulfide in the mixture. Thus, it seems that in the equilibrium process the higher polysulfides are also actively involved, and the reaction with cyclohexene proceeds through some intermediate product.

Regarding the rate of disappearance of double bond, it has been found that the rate can be empirically expressed as

$$-d\left[{}^H_>C{=}C{<}^H\right]\Big/ dt = k\left[{}^H_>C{=}C{<}^H\right]^{1/2}$$

In the reaction of sulfur and cyclohexene, the rate of formation of the product was also observed as one-half

order by Ross.[14] In rubber–sulfur reactions, the decrease of free sulfur was frequently reported as fractional order.[15-17]

Other Unsaturates with Dimethyl Tetrasulfide.— The unsaturated compounds, which have relatively simple nmr spectra for the olefinic hydrogens and are miscible with dimethyl tetrasulfide, were selected for the present study. Only in the case of maleic anhydride was benzene used as solvent. The rate of disappearance of double bond in all the unsaturated compounds was found to follow similar empirical relationship as cyclohexene except in the case of α-methylstyrene and diethyl maleate, where deviations were observed during the initial part of the reaction. The relative rate constants of the reactions, obtained from the one-half-order plot of the disappearance of double bond, show the increasing values according to the following order: diethyl maleate < maleic anhydride < methacrylonitrile ≐ methyl methacrylate < 1-methylcyclohexene < α-methylstyrene. In the case of α-methylstyrene and diethyl maleate the initial deviations were ignored. Since these are multistep reactions, the effect of substituents may be complex, but apparently more electron-rich or more polar double bonds seem to react faster.

It is difficult to analyze all of the products formed in the reaction mixture, but from the reaction with 1-methylcyclohexene the structure of the most volatile product was confirmed as 1-methylcyclohexyl methyl sulfide, which is inconsistent with the result obtained from the reaction of 1-methylcyclohexene and diphenyl tetrasulfide.[5,18] Thus the result shows that the tetrasulfide adds to olefins to give Markovnikov-type addition product. From methacrylonitrile, the most volatile product was (assigned and confirmed) found to be α-methylmercaptoisobutylonitrile.

Effect of Additives on the Rate of Saturation of the Double Bond.—The effects of radical initiators and inhibitors were investigated. In the cyclohexene reaction, though benzoquinone slightly lowers the rate, initially, the over-all rate indicates some acceleration of the reaction (Table V). The result is contradictory

TABLE V

EFFECT OF BENZOQUINONE ON REACTION OF CYCLOHEXENE
WITH DIMETHYL TETRASULFIDE[a]

Reacn time, hr	Disappearance of unsaturation, mole %	
	Benzoquinone	None
0	100	100
9.8	96.0	68.8
17.5	68.0	61.2
42.0	38.0	35.0
65.0	14.8	18.0
87.0	7.0	13.5
130.	0	5.0

[a] Molar proportion of cyclohexene and dimethyl tetrasulfide (1:1); 0.2 g of benzoquinone was added to 0.98 g of mixture.

to the radical mechanism and consistent with that reported by Ross[14] for sulfur–cyclohexene reaction. In the reaction of α-methylstyrene, benzoyl peroxide was

(14) C. W. Ross, *J. Chem. Soc.*, 2856 (1948).
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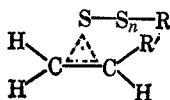(16) E. Echete, W. Scheele, and S. Sonnenberg, *Rubber Chem. Technol.*, **33**, 1051 (1960).
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found to increase the rate, whereas azobisisobutyronitrile and sulfur showed no effect and molecular oxygen had some decreasing effect (Table VI). The products of these reactions were analyzed by vpc and found to be qualitatively similar to those found in absence of additives.

TABLE VI

EFFECT OF ADDITIVES ON REACTION OF α-METHYLSTYRENE
WITH DIMETHYL TETRASULFIDE[a]

Reacn time, hr	Disappearance of unsaturation, mole %				
	BPO	AIBN	S_8	O_2	None
0	100	100	100	100	100
0.5	...	93.6	93.4	99.2	83.9
1.5	85.5	89.8	93.4	98.3	62.6
3.5	71.9	81.4	80.1	85.5	50.0
8.5	24.3	75.6	42.9	74.6	48.0
18.5	23.9	42.2	40.9	59.4	39.5
42.5	0	12.3	5.7	12.5	19.1
66.5	...	4.3	2.8	5.5	0
90.5	...	0	0	2.4	...

[a] Molar proportion of α-methylstyrene vs. dimethyl tetrasulfide (1:1); 0.05 g of BPO and AIBN, and 0.03 g of S_8 were added to each 0.94 g of the mixtures. Oxygen was passed through the similar amount of the mixture at 0° for 5 min and sealed without degassing.

A Suggestion for the Reaction Mechanism.—The dimethyl tetrasulfide can initiate polymerization of a vinyl monomer, therefore at least the first stage of the reaction may follow a free-radical reaction mechanism. The entire reaction scheme of dimethyl tetrasulfide with unsaturated compounds may also be considered as a free-radical chain reaction with relatively short chain length. Though the evidences for totally free-radical mechanism are not ironclad, at least the addition reaction step of the thiyl radicals to the double bond must be a radical reaction. The sequences of reactions, shown in Scheme II, may have reasonable importance. For polymerizable vinyl monomers a telomerization reaction which produces low molecular weight polymers with sulfide end groups is inevitable. When a hydrogen donor is present, hydrogen abstraction occurs to form reaction product A which is similar to a hypothetical addition product of RS_xH to an olefin. The same type of product can be formed by a disproportionation reaction between the two composite radicals. Any speculation on the whole reaction sequences would be difficult unless a complete product analysis is done. However, since the expected most volatile product is either type A or B, and, since no alkyl alkenyl sulfide formation is inferred during the reaction of cyclohexene, type A product may be produced mainly by hydrogen abstraction reaction.

In the case of substituted olefins like 1-methylcyclohexene and methacrylonitrile, anti-Markovnikov-type products are expected for free-radical addition reactions. Therefore the observation of the Markovnikov-type reaction product is usually considered to be strong support for an ionic addition mechanism. Ross[14] explained the formation of phenyl 1-methylcyclohexyl sulfide from diphenyl tetrasulfide and 1-methylcyclohexene as ionic addition of thiophenol (which is formed from the tetrasulfide) to the olefin.

Perhaps one way to obtain a Markovnikov-type product by free-radical addition is to assume a bridged free-radical intermediate or transition state, as proposed by

SCHEME II
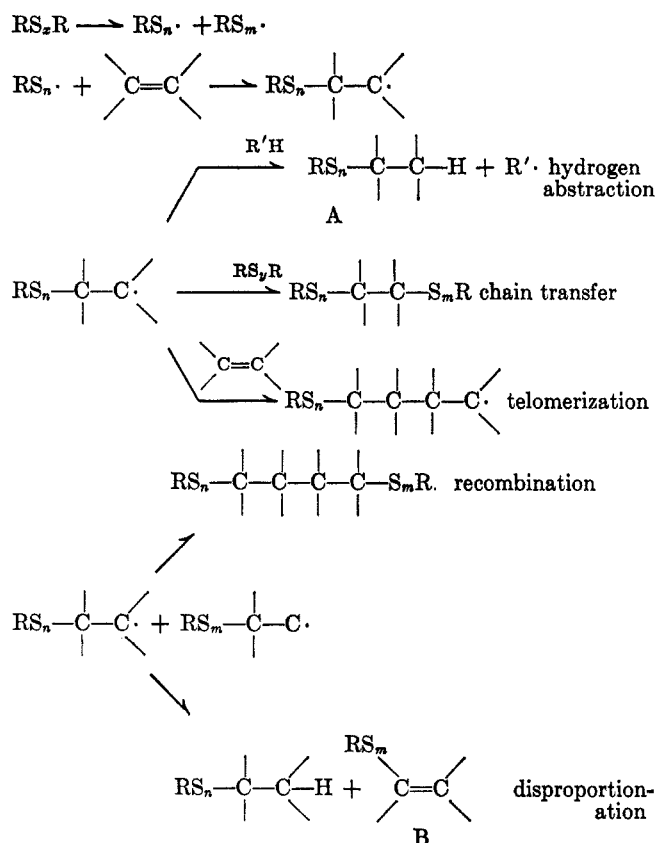
Goering[19] for halogen radical to account for the stereospecific *trans*-radical addition of HBr to 1-substituted cyclohexenes. The bridged free-radical may be represented as shown.
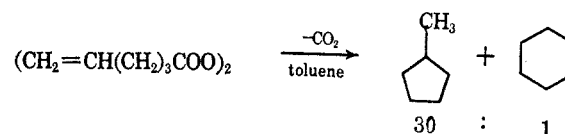

Now, in the case of dimethyl tetrasulfide and olefin reaction, we observed a slow rate of production of monosulfide. This can be attributed to slow formation of $CH_3S \cdot$ radical or to another slow process in the reaction. It is also observed that radical initiators or inhibitors show little effect on the reaction rate. Since addition reaction of $CH_3S_n \cdot$ to double bonds is relatively rapid and reversible, as is suggested by isomerization of diethyl maleate, a slow, rate-limiting step would be the following hydrogen abstraction. In the absence of a good hydrogen donor in the system, it is probably the slowest and also the sterically hindered process in the case of substituted olefins (see Scheme III, p 1516).

If the intermediate radical I could not abstract a hydrogen atom rapidly because of the steric effect of the tertiary carbon radical, which should abstract a hydrogen atom from allylic position of other olefin molecule, there is a possibility of forming radical type II provided that steric hindrance at the substituted carbon atom is not too large. Abstraction of hydrogen by radical II would be faster than that by radical I. Thus the kinetically favored process for

trapping of less favorable radical intermediate II may be accomplished.

Lamb, *et al.*,[20] studied the decomposition of 6-heptenoyl peroxide in toluene and found methylcyclopentane as a major product. In this case also, the un-


favorable radical is kinetically trapped owing to the conformational effect of the intermediate radical.[21-23] Oswald[24] observed that free-radical addition of thiol to diallyl maleate produced a Markovnikov-type addition product as a minor one, even in the presence of a good hydrogen donor, namely thiol.
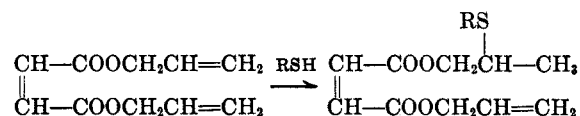
Since there is a 2–3-kcal/mole difference between the ground-state energies of Markovnikov and anti-Markovnikov products,[25] the selectivity of product formation may arise from the kinetic preference and probably not from thermodynamical one.

Isomerization of the intermediate radicals is another possibility to be considered.
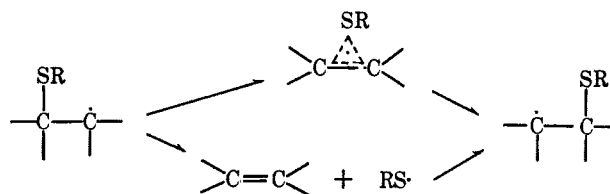
Two alternatives leading to isomerization may be involved. One is 1,2 shift and the other is a dissociation followed by addition. In this case the latter is perhaps more likely.

The ionic mechanisms involving possible polysulfenyl cations have not been ruled out. A further consideration is required for rationalizing any of the above possibilities.

Experimental Section

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(20) R. C. Lamb, P. W. Ayers, and M. K. Toney, *ibid.*, **85**, 3483 (1963).
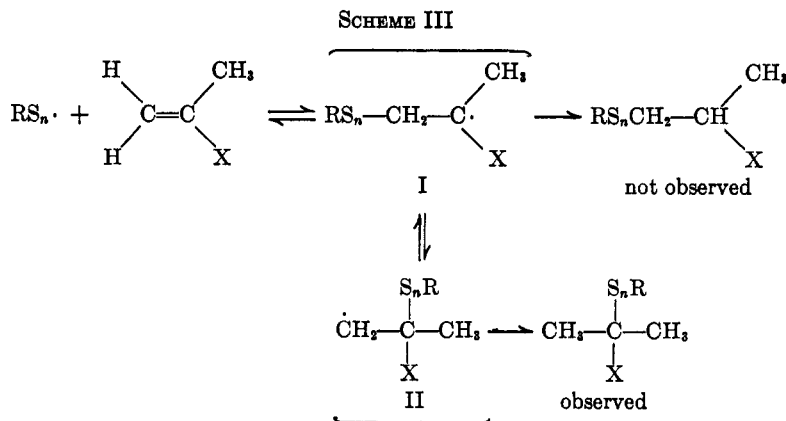
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(25) H. Mackle, *Tetrahedron*, **19**, 1159 (1963).

SCHEME III

and cyclohexene (Eastman Organic Chemicals), bp 83–84° (760 mm), were distilled under nitrogen. Cyclohexane (Matheson Coleman and Bell), maleic anhydride (Matheson Coleman and Bell), and benzene (Baker and Adamson) were used without further purification. Azobisisobutyronitrile was recrystallized twice from an ether–chloroform mixture.

Polymerization of Methyl Methacrylate and Acrylonitrile.—The mixtures of monomer, solvent, dimethyl tetrasulfide, and/or azobisisobutylonitrile were placed in Pyrex glass ampoules, where they were degassed three times by using a cycle of freezing with liquid nitrogen, pumping off to 10^{-2} mm, thawing, and nitrogen gas flashing. The evacuated ampoules were finally sealed off and allowed to immerse for the desired period of time in a dark oil bath which was kept at constant required temperature ($\pm 0.1°$). The polymers were precipitated with a large amount of methanol and collected on sintered glass filters which were weighed previously. The amount of polymer determined by weighing the sample after drying for 24 hr under vacuum at room temperature and for 2 days in a vacuum oven at 55°. These values were used for calculation of per cent conversion to polymer. The percent conversions were about 2 to 4% in most cases.

Number-average degree of polymerization of polyacrylonitrile was calculated by employing the equation of Onyon.[26] Intrinsic

$$\log \bar{P}_n = 2.825 + 1.33 \log (\eta)$$

viscosities (η) of polyacrylonitrile were measured in N,N-dimethylformamide at 25°.

Kinetic Runs.—Equimolar quantity, unless otherwise noted, of unsaturated compound and a dimethyl polysulfide were placed in a modified nmr sample tube along with the small amount of tetramethylsilane which was sealed in a capillary tube, degassed accordingly, and sealed off. In the case of maleic anhydride, benzene was used as a solvent. Disappearance of unsaturation, appearance of various methyl polysulfides, and cis–trans isomerization in the case of diethyl maleate, were followed by nmr spectroscopy. (Varian Model A-60 A was used.) Reactions were carried out in the dark, in a constant-temperature bath. Resonance peak positions of methyl groups in the polysulfides are τ 6.86 (hexasulfide), 6.88 (pentasulfide), 6.91 (tetrasulfide), 7.02 (trisulfide), 7.18 (disulfide).

Cyclohexene, methyl methacrylate, methacrylonitrile and α-methylstyrene show doublet (of multiplets) resonance peaks of olefinic hydrogens, 1-methylcyclohexene shows broad singlet and maleic anhydride and diethyl maleate shows singlets at around τ 3–4. Areas under the resonance peaks were measured and compared with that of tetramethylsilane.

The resonance peak of the olefinic hydrogens of diethyl maleate appears at τ 3.53 (neat), and that of the fumarate appears at 3.05 (neat). In the presence of dimethyl sulfides the positions of these peaks shift somewhat to the low τ value, but they are easily recognizable. The molar ratios of the maleate and the fumarate were calculated by the integrated areas under each of the resonance peaks.

Product Analysis. A. Cyclohexene–Dimethyl Tetrasulfide. —Cyclohexene and dimethyl tetrasulfide (molar proportion 2:1) were placed in a Pyrex glass ampoule, degassed and sealed off. The ampoule was heated at 130° for about 200 hr. Then it was removed from the bath, quenched, and opened. The reaction

mixture was fractionated into six fractions and a residue: fraction I [bp 54–65° (4 mm)], II [bp 65–72° (4 mm)], III [bp 72–100° (4 mm)], IV [bp 100–120° (4 mm)], V [bp 120° (4 mm)], and VI [bp 125–135° (0.5 mm)]. The volatile fractions were analyzed by vpc and nmr spectroscopy. In vpc analysis, a silicone gum column was installed in an F & M Model 720, and the following conditions were maintained throughout the analysis: injection port temperature, 175°; detector temperature, 260°; column temperature, started at 65° and programmed 10°/min up to 210°; the carrier gas (He) pressure, 30 psig; flow rate, 70 ml/min. Two major vpc peaks owing to products were observed other than those of dimethyl sulfides. The temperatures at which the peaks owing to dimethyl sulfides appear are dimethyl disulfide, 92–95°; dimethyl trisulfide, 127–129°; and dimethyl tetrasulfide, 164–169°.

The fraction I mainly contained product 1 (appearance temperature 139–142°) and showed a distinct CH_3S resonance peak (τ 7.52) in the nmr spectrum. Thus the product 1 was considered to be methyl cyclohexyl monosulfide. Fraction IV contained mainly product 2 (appearance temperature 179–181°) and dimethyl trisulfide. There was no indication of the presence of dimethyl disulfide but the nmr spectrum of the fraction showed a significant CH_3S_2 resonance peak (τ 7.10). Therefore the product 2 was assigned as methyl cyclohexyl disulfide. The viscous residue showed neither CH_3S_n resonance peak nor olefinic hydrogen peaks but only CH_2 resonance peaks in CS_2 solution. The residue was assumed to consist of mainly the polymer of cyclohexene in which sulfur chains might be incorporated.

Dimethyl tetrasulfide and cyclohexene (1:1 molar ratio) were mixed and divided into six small Pyrex ampoules and sealed in the presence of air, and heated at 130° for 1 to 120 hr. The reaction mixtures were again analyzed by vpc and nmr technique. The rate of disappearance of double bond measured by nmr is the same as that of the disappearance of cyclohexene measured by vpc. This fact indicates the absence of cyclohexenyl-type compounds. The rate of formation of products 1 and 2 was also obtained (Table IV).

B. 1-Methylcyclohexene–Dimethyl Tetrasulfide.—Dimethyl tetrasulfide and 1-methylcyclohexene (1:1 molar ratio) were degassed and sealed in a Pyrex ampoule. After heating for 6 days at 130°, the reaction mixture was fractionated: fraction I [bp 25–65° (2 mm)], II [bp 65–80° (2 mm)], III [bp 80–117° (2 mm)], and IV [bp 117–151° (2 mm)]. Two reaction products were observed by vpc (appearance temperatures are 147–150° for 1 and 181–183° for 2). Fraction I was treated with excess LiAlH₄ to remove dimethyl polysulfides by hydrogenolysis to methane thiol. Product 1 was separated in relatively pure form, and the nmr spectrum of the product 1 showed a CH_3S peak (τ 7.67) along with a singlet CH_3 peak (τ 8.32) and a methylene peak centered around τ 8.05. Relative areas under the peaks were 3:3:10, respectively. Thus, product 1 was assigned as 1-methylcyclohexyl methyl monosulfide. To confirm the structure of the product 1, an authentic sample of 1-methylcyclohexyl methyl monosulfide was prepared by addition of methanethiol to 1-methylcyclohexene in the presence of 75% H_2SO_4.[27] The authentic sample and the product 1 show exactly the same vpc appearance temperature and nmr spectrum.

C. Methacrylonitrile–Dimethyl Tetrasulfide.—Methacrylonitrile and dimethyl tetrasulfide (2:1 molar ratio) were similarly

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(27) V. N. Ipatieff, H. Pines, and B. S. Friedman, J. Am. Chem. Soc., **60**, 2731 (1938).

degassed and heated at 130° in an ampoule for 200 hr. The reaction mixture was fractionated: fraction I [bp 22–35° (2 mm)], II [bp 35–65° (2 mm)], III [bp 65–120° (2 mm)]. By vpc analysis, it was revealed that the products of this reaction consist of one predominant product (1) appearance temperature 113°) along with several minor products.

Fraction I contained essentially the product 1 with a small amount of dimethyl trisulfide, and the nmr spectrum of the fraction showed a singlet CH_3 peak (τ 8.00) with relative area 2 and a singlet CH_3S peak (τ 7.34) with relative area 1; hence the product 1 was assigned as α-methylmercaptoisobutylonitrile. The independent synthesis of this compound from sodium salt of methanethiol with α-chlorobutylonitrile confirmed the structure.

Free-Radical Chlorination Reactions of Iodobenzene Dichloride

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The photoinitiated chlorination of several substituted alkanes with iodobenzene dichloride (IBD) showed product isomer distributions which were remarkably similar to those obtained for halogenation with molecular chlorine. IBD had been previously shown to halogenate 2,3-dimethylbutyl by a mechanism which did not involve chlorine radicals. A more detailed investigation of the mechanism of IBD chlorination, by studying its selectivity, relative reactivity, and primary deuterium isotope effect, has confirmed the proposal that the PhICl radical is the abstracting species in the radical halogenation reactions of substituted and unsubstituted hydrocarbons. The anomalous results for the halogenation of negatively substituted alkanes are attributed to polar effects on the radical-abstraction reaction.

During the course of the investigation of solvent effects on the photoinitiated chlorination of 2,3-dimethylbutane, Russell reported that when iodobenzene was used as solvent for the reaction the selectivity toward hydrogen abstraction for tertiary to primary hydrogen was 31/1 while for molecular chlorine in carbon tetrachloride a value of 5/1 was observed.[2] It was noted that the yields of alkyl halides obtained were low. To explain these results he proposed that the chain-carrying species in the reaction were PhICl and Cl· radicals, and that PhICl must be an extremely selective hydrogen-abstracting radical.

In an attempt to generate PhICl radicals, Banks, Huyser, and Kleinburg photolized iodobenzene dichloride (IBD) in 2,3-dimethylbutane[3] and noted that the radical selectivity was indeed very high, since they found that no primary halide resulted from the chlorination. They proposed PhICl as the sole chain-carrying species.

We were interested in this halogenating reagent both for its high selectivity, and as a means of studying polar effects in hydrogen-abstraction reactions using iodobenzene dichloride and substituted iodobenzene dichlorides. Preliminary examination of the products of chlorination of several negatively substituted alkanes with IBD showed isomer distributions which were almost identical with those reported in the literature for halogenation with molecular chlorine. The results of a more detailed examination of these reactions is the purpose of this report.

Discussion and Results

Products of Photoinitiated Halogenation.—Examination of the products of photochlorination of cyclo-

(1) Presented in part at the 49th National Meeting of the Chemical Institute of Canada, Saskatoon, 1966.

hexane with IBD (40°, in carbon tetrachloride) showed high yields of cyclohexyl chloride, and a material balance for the reaction products was in agreement with that obtained by Huyser[3] (see Table I). In addition

Table I

Products of Photoinitiated Reactions

Cyclohexane with IBD
(1:10 Mole Ratio, 40°, CCl_4 Solvent)

IBD	$C_6H_{11}Cl$	C_6H_5I	HCl	Other products[a]
1.04	...	...	1.09	...
1.05	1.09	1.07	...	<0.05
0.960	0.860	0.879	...	<0.05
0.989	0.963	0.943	...	<0.05

1-Chlorobutane with IBD
(1:10 Mole Ratio, 40°, CCl_4 Solvent)

IBD	HCl	$C_4H_8Cl_2$ (all isomers)	C_6H_5I	C_6H_5Cl	Photo-rearrangement product	Other products[a]
1.22	1.04	...	...	...	...	...
1.15	1.05	...	...	...	...	...
1.20	...	0.567	0.765	0.038	0.362	<0.1
1.16	...	0.523	0.777	0.034	0.341	<0.1
1.20	...	0.548	0.782	0.039	0.340	<0.1
1.19	...	0.553	0.749	0.039	0.331	<0.1

[a] Yields of unidentified products were estimated by comparing their integrated areas of glpc chromatograms with those of the chlorinated 1-chlorobutanes.

to the cyclohexyl chloride reported by Huyser, small amounts of chlorobenzene and cyclohexyl iodide were obtained as well as small amounts of products resulting from the photolysis and thermolysis of IBD itself.[4]

(2) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958).
(3) D. F. Banks, E. S. Huyser, and J. Kleinburg, *J. Org. Chem.*, **29**, 3692 (1964).
(4) Unpublished work from this laboratory.