TABLE II

hkl	d_0	d_c	I_0[a]	d_0	I_0 for Ba_2CaWO_6[b]
111	4.82	4.815	m+	4.84	22
200	4.17	4.170	m−	4.20	1
220	2.948	2.949	s+	2.97	100
311	2.516	2.514	m	2.53	9
222	2.403	2.408	w	2.42	4
400	2.082	2.085	s−	2.10	30
331	1.913	1.913	m−	1.925	4
420	1.864	1.865	m		..
422	1.702	1.702	s	1.713	37
333	1.604	1.605	m	1.615	4
440	1.474	1.474	m+	1.483	15
531	1.411	1.410	m−	1.418	4
442	1.391	1.390	w		..
620	1.320	1.319	m+	1.327	15
533	1.272	1.272	w−	1.279	1
622	1.258	1.257	w−	1.265	1
444	1.204	1.204	w	1.211	6
711	1.168	1.168	w	1.175	3
640	1.157	1.157	w−		..
642	1.116	1.115	m+	1.121	22

[a] s = strong, m = moderate, w = weak. [b] Data taken from A.S.T.M. card 6-0400.

X-Ray Analysis.—The compounds were investigated in powder form in hermetically sealed Lindemann glass capillaries in order to avoid any hydrolysis. Copper radiation (λ = 1.5418) was used, filtering the β-radiation with a nickel filter. In Table II are summarized the observed and calculated interplanar spacings as well as the observed[2] intensities of Ba_2CaWO_6 for comparison. The lattice constant for $Sr_3TaO_{5.5}$ of 8.34 Å. is very close to that for Ba_2CaWO_6 of 8.39 Å. Steward and Rooksby[2] found that this compound belongs to the cubic $(NH_4)_3FeF_6$-type which crystallizes in the space group O_h^5. The observed diffraction lines have either all odd or all even indices, indicating a face-centered cubic structure. Since the patterns of $Sr_3TaO_{5.5}$ and Ba_2CaWO_6 are essentially identical and since the concordance of the intensities is good, it can be stated that $Sr_3TaO_{5.5}$ crystallizes in the same structure, that is, in the $(NH_4)_3FeF_6$-type. In Table III are given the observed and calculated interplanar spacings for the compounds Ba_2LaTaO_6 with a_0 = 8.62 Å., Sr_2LaTaO_6 with a_0 = 8.27 Å. and $Ba_3TaO_{5.5}$ with a_0 = 8.69 Å.

TABLE III

OBSERVED AND CALCULATED INTERPLANAR SPACINGS OF

	$Ba_3TaO_{5.5}$			Ba_2LaTaO_6			Sr_2LaTaO_6		
hkl	d_0	d_c	I_0	d_0	d_c	I_0	d_0	d_c	I_0
111	5.01	5.017	m	4.98	4.97	w	4.77	4.77	m
200	4.34	4.345	w	4.32	4.31	w	4.13	4.13	m
220	3.07	3.072	s+	3.06	3.045	s+	2.92	2.921	s+
311	2.618	2.620	w−	2.60	2.599	w−	2.49	2.492	m−
222		2.509		2.50	2.485	w−	2.40	2.385	w−
400	2.170	2.172	s−	2.16	2.155	s−	2.06	2.062	s−
331	1.992	1.994	m	1.97	1.977	w−	1.90	1.896	w
420		1.943		1.93	1.927	w−	1.86	1.849	w
422	1.772	1.774	s	1.76	1.760	s	1.69	1.689	s
333	1.671	1.672	m	1.66	1.658	w−	1.59	1.590	m
440	1.534	1.536	m+	1.53	1.522	m+	1.46	1.461	m+
531	1.468	1.469	w	1.45	1.457	w−	1.39	1.398	w
442		1.448			1.436		1.38	1.378	w−
620	1.373	1.374	m+	1.36	1.361	m+	1.31	1.306	w
533	1.323	1.325	w		1.313		1.26	1.261	w−
622		1.310			1.300			1.247	
444	1.253	1.254	w	1.25	1.243	w	1.19	1.192	w−
711	1.217	1.217	w=		1.207			1.158	
640		1.205			1.195			1.136	
642		1.160	m	1.15	1.151	m+		1.104	

Discussion

The reaction between stoichiometric amounts of Ta_2O_5 and $SrCO_3$ or $BaCO_3$ to form $Me_3TaO_{5.5}$ as a pure phase, indicates that, in the case of the $(NH_4)_3FeF_6$ structure, there might be a similar range of anion deficient structures as has been observed for the perovskites. In the case of tungsten and uranium, compounds like $Ba_3WO_{5.5}$ and $Ba_3UO_{5.5}$ can be postulated with the transition elements in the 5-valent oxidation state.

Since there are four molecules per cell, a total of two oxygens are missing in the unit cell of the compound $Sr_3TaO_{5.5}$. The question as to whether these vacancies are randomly distributed or located at definite lattice sites can only be answered by a more precise X-ray investigation.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Organic Disulfides as Initiators of Polymerization. Part II[1]

BY T. FERINGTON[2] AND A. V. TOBOLSKY

RECEIVED JULY 31, 1957

The study of the compound tetramethylthiuram disulfide (TMTD) as an initiator of the polymerization of methyl methacrylate has been extended to 60 and 80°. The experimental points are fit by the equation $R'_i/(\text{cat.}) = 4.80 \times 10^{14} \exp(-31.6\ \text{kcal.}/RT)$. This equation falls in the same range as the similar expression for, *e.g.*, benzoyl peroxide, although the S–S bond is much stronger than the O–O bond. TMTD also has a retarding effect which was studied at 30° where the initiating effect does not appear. Retardation is due to radical attack on the TMTD molecule to produce an inhibiting TMTD radical residue. Evidence on the photoactivity of TMTD also was obtained. Various polar reagents were studied as to their effect on the rate of generation of radicals by TMTD but no pronounced change was found. A comparison with vulcanization data for TMTD indicates similar primary steps in vulcanization and polymerization by this compound. Tetramethylthiuram monosulfide (TMTM) was studied in the same way as TMTD at 70, 80, 90°. No retardation was found. The experimental points for initiation were fit by the equation $(R'_i/\text{cat.}) = 9.0 \times 10^{11} \exp(-29.4\ \text{kcal.}/RT)$. The energy of activation is very similar to that for TMTD. Experimental observations on the photoactivity of TMTM are given. Dipentamethylenethiuram tetrasulfide was found to have a purely retarding behavior with methyl methacrylate. Diphenyl disulfide, while much less active than TMTD, shows a very similar combination of initiating and retarding ability at 100°. A mechanism is presented which fits the above observations. Retardation is due to polysulfide radical species, $RS_x\cdot$ $(x > 1)$ and initiation through the intermediate radical $RS\cdot$. In the case of thiuram compounds this latter is unstable and further decomposes to $CS_2 + (CH_3)N\cdot$. This mechanism is consistent with most of the observed data on thiuram vulcanization.

Introduction

In the previous publication the decomposition of the compound tetramethylthiuram disulfide (TMTD) was studied at 70° in the presence of the common vinyl monomers styrene and methyl

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[1] Part I is T. Ferington and A. V. Tobolsky, THIS JOURNAL, **77**, 4510 (1955).

[2] This article is based upon a dissertation submitted by Thomas Ferington in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

methacrylate. In the present paper we report more extensive studies on TMTD as well as on related compounds. The monomer methyl methacrylate has been used exclusively in these studies since it gives a higher rate of polymerization for a given catalyst than does styrene, thus lower catalyst concentrations can be studied. With this exception the experimental procedure was the same as that described in Part I.[1]

Experimental Results

Values for R_p were obtained at 60 and 80°. These are recorded in Table I and the variation of R_p with catalyst concentration made more clear in Figs. 1 and 2.

TABLE I

POLYMERIZATION OF METHYL METHACRYLATE INITIATED BY TMTD

A 60°		B 80°	
(TMTD) × 10^3, mole/l.	R_p[a] × 10^5, mole/l. sec.	(TMTD) × 10^4, mole/l.	R_p[a] × 10^5, mole/l. sec.
13.5	2.69	8.47	11.4
7.88	2.90	5.32	10.3
5.40	2.56	3.39	8.14
4.38	2.97	2.13	6.98
3.15	2.86	1.35	6.03
2.16	2.62	0.853	5.13
1.75	2.72	.542	4.04
1.26	2.86	.341	3.40
0.864	2.09	.216	2.47
.700	2.00	.136	2.12
.346	1.82		
.280	1.42		
.202	1.29		
.0945	1.01		
.0806	0.88		

[a] Corrected for thermal polymerization using the relationship

$$R^2_{p,\,obs} = R^2_{p,\,th} + R^2_{p,\,cat} \qquad (1)$$

$R_{p,\,th}$ = thermal rate of polymerization in absence of catalyst
$R_{p,\,cat}$ = rate of polymerization due to effect of catalyst only
$R_{p,\,obsd}$ = rate of polymerization observed
$R_{p,\,th}$ = 0.27×10^{-5} at 60°
0.98×10^{-5} at 80°

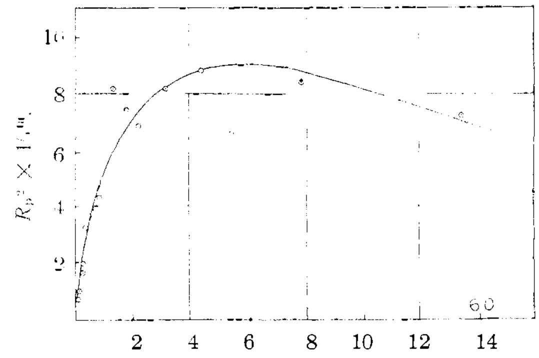

Fig. 1.—Rate of polymerization of methyl methacrylate TMTD at 60°.

From Fig. 1 one calculates $R_i'/(\text{cat})$ by drawing a tangent to the "low catalyst" portion of the curve,[1] using the values $A' = 64^3$ and (M) = 8.95 and substituting in equation 2 of ref. 1.

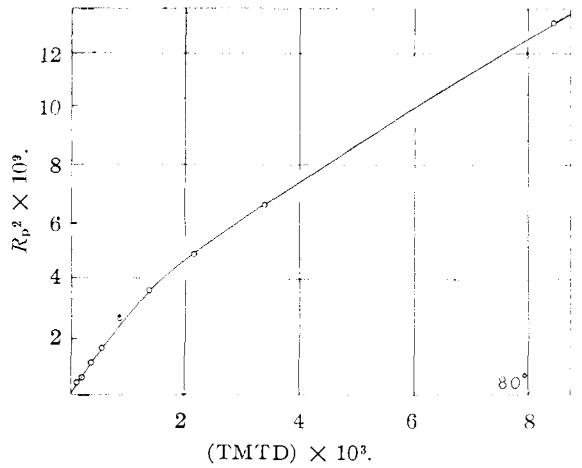

Fig. 2.—Rate of polymerization of methyl methacrylate with TMTD at 80°.

The value for $R_i'/(\text{cat})$ at 80° is obtained from Fig. 2 in the same fashion using $A' = 30.5^3$ and (M) = 8.72. These results are presented in Table II.

TABLE II

RATES OF INITIATION BY TMTD IN METHYL METHACRYLATE

Temp., °C.	$R_i'/(\text{cat})$
60	1.4×10^{-6}
70	5.4×10^{-6}[a]
80	26.2×10^{-6}

[a] This value reported in ref. 1.

When the data of Table II were made into an Arrhenius plot a good straight line was obtained whose equation corresponded to the relation

$$R'_i/(\text{cat}) = 4.80 \times 10^{14} \exp\left(\frac{-31.6 \text{ kcal.}}{RT}\right) \qquad (2)$$

The energy of activation obtained (31.6) falls in the usual range for organic peroxides when they are used as initiators of polymerization. For example, for benzoyl peroxide

$$R'_i/(\text{cat}) = 3.99 \times 10^{14} \exp(-30.0 \text{ kcal.}/RT) \qquad (3)$$

This close correspondence is somewhat surprising in view of the greatly different relationships in bond strengths between peroxides and disulfides.

Other low values have been noted in sulfur containing molecules. Gee[4] calculated a value of 35 kcal. for the breaking of the S–S bond in polymeric sulfur from viscosity data. Braye, *et al.*,[5] assign a value of 51 kcal. to the C–S bond in $C_6H_5CH_2CCH_3$ on the basis of their kinetic measurements in the vapor phase. In this last case there seems no question that a simple cleavage is involved.

TMTD as a Retarder.—In the previous communication[1] it was reported that TMTD acted as a retarder for the polymerization of methyl methacrylate by azobisisobutyronitrile (Azo-I) at 30°. This work has been continued in the hope of separating the initiating and retarding effects which occur simultaneously at higher temperatures.

The initial experiments showed a curve of R_p *vs.*

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(3) T. E. Ferington and A. V. Tobolsky, *J. Colloid Sci.*, **10**, 536 (1955).

(4) G. Gee, *Trans. Faraday Soc.*, **48**, 515 (1952).

(5) E. Braye, A. Sehon and D. Darwent, THIS JOURNAL, **77**, 5282 (1952).

(TMTD) at constant Azo-I which was very similar to those obtained at higher temperatures. These results are presented in Table IIIA and Fig. 3. This unexpected behavior together with the observation that the rate of polymerization of methyl methacrylate at 30° with (TMTD) = 4.15×10^{-3} mole/l. was 1.35×10^{-5} mole/l. sec. while the value calculated from eq. 3 is 3.09×10^{-6} mole/l. sec. soon led to the observation that TMTD is decomposed by visible light. The rate of this photo decomposition is large compared to the thermal rate at these lower temperatures but checks on the previous results at 60° and higher showed that excluding light from those samples made no significant change.

The photo effect may explain the somewhat greater scatter of the points at 60° but does not affect the over-all shape of the graph.

TABLE III

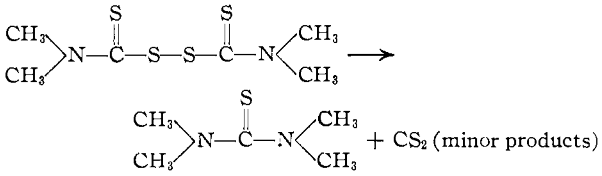
POLYMERIZATION OF METHYL METHACRYLATE BY AZOBISISOBUTYRONITRILE AT 30° IN THE PRESENCE OF TMTD

A: In the presence of light (Azo) = 2.03×10^{-3} mole/l. (TMTD) $\times 10^2$	 $R_p \times 10^6$	B: In the absence of light (Azo) = 3.35×10^{-3} mole/l. (TMTD) $\times 10^2$	 $R_p \times 10^6$
2.02	4.15	2.98	1.83
1.61	4.65	2.31	1.88
1.21	5.69	1.73	2.42
0.808	9.66	1.66	2.75
.404	11.69	1.15	2.82
.0	8.20	0.584	3.34
		.291	4.71
		.132	6.48
		.066	6.68
		.0	10.4

Separation of the initiating and retarding effects was achieved by making up the polymerization tubes by weighing the TMTD into each individual tube and then not dissolving it in the methyl methacrylate until the tubes were degassed, sealed and wrapped in aluminum foil to keep out the light. When this procedure was followed a purely retarding effect was observed. The results are given in Table IIIB and Fig. 3.

A plot of log R_p *vs.* log (TMTD) from the values of Table IIIB was made in the hope of gaining some information as to the nature of the retardation reaction shown in Fig. 3. The points were linear within experimental error over the entire concentration range studied; however, the slope, −0.43, had no obvious interpretation in terms of a simple kinetic picture.

Effect of Environment on Rate of Decomposition of TMTD.—Earlier workers who studied the role of TMTD in vulcanization[6,7] found that the rate of decomposition of this compound was dependent on the presence of other materials. For example, Bloomfield[4] followed the pyrolysis reaction



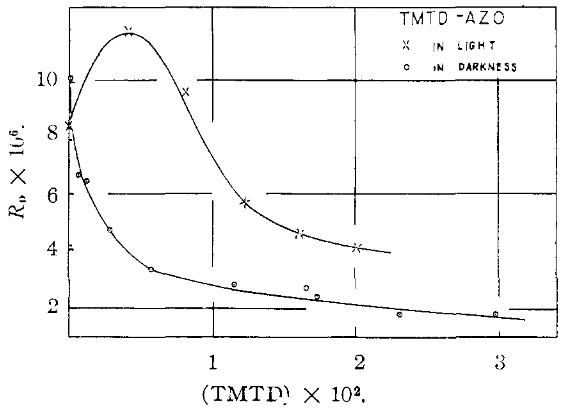


Fig. 3.—Polymerization of methyl methacrylate by azobisisobutyronitrile at 30° in the presence of TMTD. (Azo) = 2.03×10^{-3} mole/l. run in presence of light. (Azo) = 3.4×10^{-3} mole/l. run in dark.

by measuring the rate of evolution of CS_2. At 100° he found the rate to be 0.03% of the theoretical yield per hour, while if the TMTD was intimately mixed with rubber, the rate was 4% per hour. Scheele, *et al.*,[7] found that the rate of decomposition of TMTD in boiling acetone (56.5°) was much faster than in boiling cyclohexane (80.1°). Zinc dimethyldithiocarbamate (ZMTC) was also very effective in accelerating the decomposition in acetone but much less so in cyclohexane, ZMTC is formed by the reaction of ZnO with TMTD. In the vulcanization of rubber with TMTD it also has been found that ZnO accelerates the vulcanization reaction and that TMTD and S_8 interact to form a much faster vulcanizing system than S_8 alone.

It seemed desirable to test whether these observations of interaction of TMTD with other materials carried over to the case of vinyl-free radical polymerization by TMTD. A possible analog of the case of decompositions in acetone and cyclohexane was observed in that the value of $R_i'/(\text{cat})$ at 70° for styrene was less than that for the more polar monomer methyl methacrylate (Table IV).

TABLE IV

RATES OF INITIATION BY TMTD AT 70°

Monomer	$Ri'/(\text{cat})$
Styrene	3.34×10^{-6}
Methyl methacrylate	5.4×10^{-6}

However, a similar effect is also observed with benzoyl peroxide in these two monomers. Other studies of the effects of added reagents showed only small changes in rate of polymerization. In the case of the polar materials acetic acid and pyridine a very considerable amount of additive produced only a small decrease in the observed rate of polymerization. ZnO produced no effect. (In this experiment the finely powdered reagent grade ZnO was added to the polymerization samples which were degassed and sealed in the usual manner. The tubes were mounted on a shaker during the polymerization to get the best possible mixing of ZnO, monomer and catalyst.) S_8, rather than showing an accelerating effect, showed its usual retarding ability.

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(6) G. Bloomfield, *J. Soc. Chem. Ind. (London)*, **68**, 66 (1949).

(7) W. Scheele, O. Lorenz and W. Dummer, *Rubber Chem. and Tech.*, **29**, 1 (1956).

TABLE V

EFFECT OF ADDED REAGENTS ON DECOMPOSITION OF TMTD AS MEASURED BY POLYMERIZATION OF METHYL METHACRYLATE

Added reagent	(TMTD), mole/l.	T, °C.	R_p
Glacial acetic acid (10% by vol.)	8.19×10^{-3}	30	1.75×10^{-6}
Pyridine (10% by vol.)	8.19×10^{-3}	30	2.1×10^{-6}
None	8.19×10^{-3}	30	2.6×10^{-6}
S_8 (rhombic) (0.0030 g.)	8.33×10^{-3}	70	5.14×10^{-5}
None	8.33×10^{-3}	70	6.93×10^{-5}
None	8.33×10^{-3}	70	6.93×10^{-5}
ZnO (0.030 g.)	1.30×10^{-3}	70	5.5×10^{-5}
None	1.30×10^{-3}	70	5.6×10^{-5}
Tetramethylthiuram-monosulfide, 3.84×10^{-2} mole/l.	3.33×10^{-2}	70	6.64×10^{-5}
None	3.33×10^{-2}	70	4.60×10^{-5}

Tetramethylthiuram monosulfide (TMTM) has been mentioned by earlier authors[8] as an inhibitor in the vulcanization of rubber by TMTD and similarly in the polymerization of chloroprene by TMTD.[9] Although we had earlier observed that TMTM is an initiator of vinyl polymerization in its own right as was also found independently by Kern,[10] it seemed desirable to test the mixed mono and disulfides. This mixture gave a rate of polymerization of 6.64×10^{-5} mole/l. sec. at 70° in the absence of light. The predicted rate if each catalyst acted independently of the other would be 5.08×10^{-5} mole/l. sec. since the rates of initiation should be additive. The observed rate is thus somewhat higher than expected rather than showing any inhibition effect.

All of the experiments in this section were suggested by observations on vulcanizing rubber systems. Although the conditions of vinyl polymerization are quite different from those of vulcanization—liquid system *vs.* solid, 79° *vs.* 125°, etc.—it was hoped that at least some of the observations would carry over since both processes are presumed to follow a free radical mechanism. None of these interactions was found in the case of vinyl polymerization, and it appears that they do not affect the primary step of generation of radicals.

Comparison with Other Experimental Results.—While this work was in progress, T. Otsu[11] published experimental results on a survey of a number of organic disulfides as thermal and photo initiators of polymerization. His data for TMTD are at a catalyst concentration somewhat higher than that corresponding to the initial linear portion of the R_p^2 *vs.* (cat) curve which we have been most concerned with; however, his results may still be compared with ours. For example, at 70° one may obtain from his data that $R_i'/(\text{cat})$ is 2.20×10^{-6}/sec. when the TMTD concentration is 1.33×10^{-2} mole/l. Our experimental result at this catalyst concentration gives $R_i'/(\text{cat})$ as 2.40×10^{-6}/sec. This is quite a satisfactory check.

Extensive kinetic studies of the action of TMTD in the vulcanization of rubber have been made by Scheele and co-workers. Their studies were generally carried out at higher temperatures than the present work but one set of experiments is reported for 87°.[12] A comparison of our results with theirs is of interest since it bears on the validity of making interpretations regarding the vulcanization behavior of TMTD and other rubber chemicals from their behavior in vinyl polymerization.

Scheele, *et al.*,[11] followed the rate of disappearance of TMTD from a vulcanizing mixture at 87°. Using their observed rate law one can calculate a half-life for the disappearance of TMTD of 481 min. under these conditions. If our experimental results in the range 60–80° are extrapolated to 87° and if one assumes that each radical produced initiates a polymer chain, the calculated half-life for the unimolecular decomposition of TMTD will be 462 min. (Uncomplicated unimolecular decomposition is assumed to take place in the concentration range covered by the initial linear portion of the R_p^2 *vs.* (cat) curve.) The good agreement between the two calculated half-lives is evidence that the primary step is the same in both cases.

Scheele also found that the disappearance of TMTD was first order until 80–90% of the TMTD had vanished. This is in accord with our view of initiation by homolytic cleavage.

Tetramethylthiuram Monosulfide.—Although TMTM has been listed by several authors[8,9] as an inhibitor for vulcanization by TMTD, it was found by us and by Kern[10] that it is an initiator of polymerization of vinyl monomers. As with many sulfur compounds[10,13] the initiating activity can come from either thermal splitting of the molecule to form radicals or a photo-cleavage. TMTM is somewhat unusual in the large amount of homolytic cleavage caused by visible light.

Experimental

"Thionex" made by E. I. du Pont de Nemours and Company, Rubber Chemicals Division, was recrystallized 3 times from isopropyl alcohol. This product was ground to a fine powder and extracted, first with cold petroleum ether and then with cold diethyl ether. Finally another recrystallization from isopropyl alcohol was made. As with TMTD, the commercial product was found to have inhibiting impurities which had to be removed before meaningful quantitative results could be obtained.

The photo-activity of TMTM is much higher than that of TMTD. It seemed possible that this enhanced activity was due to some higher sulfide which was present as an impurity. However, when a study of extent of conversion with time was made on the purified TMTM, a linear relation was found to hold to higher than 20% conversion. This result is shown in Fig. 4. If a minor impurity had been present and acting as the active principle, a curved line should have resulted in these experiments as the rate of polymerization decreased due to the depletion of this impurity.

When studies of thermal cleavage of TMTM were made, the samples were protected from the light in this way. The catalyst was weighed into each tube separately, the tubes wrapped with aluminum foil and the monomer added only after the room lights were out and the shades down. The work was done in the evening after dark. The tubes were degassed and sealed off while the room was completely darkened except for a 7.5 watt bulb which was 15 feet away and

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[8] D. Craig, A. Juve and W. Davidson, *J. Polymer Sci.*, **5**, 709 (1950).

[9] H. Kaneko, *J. Soc. Rubber Ind. Japan*, **17**, 393 (1944).

[10] R. Kern, THIS JOURNAL, **77**, 1382 (1955).

[11] T. Otsu, *J. Polymer Sci.*, **21**, 559 (1956).

[12] W. Scheele, O. Lorenz and W. Dummer, *Rubber Chem. and Tech.*, **29**, 15 (1956).

[13] S. Birch, T. Cullum and R. Dean, *J. Inst. Petroleum*, **39**, 206 (1953).

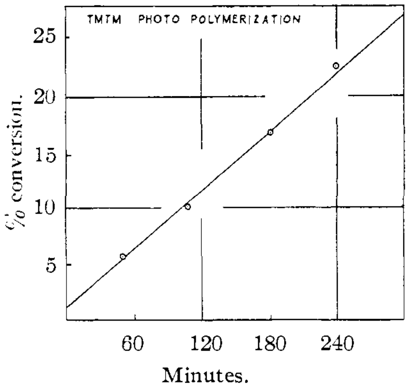

Fig. 4.—Photoinitiation by TMTM in methyl methacrylate. (TMTM) = 4.74×10^{-3} moles/l.

completely shielded by a towel. The thermostat baths were also in the darkroom so the samples were not exposed to light until after the polymer had been precipitated.

The success of this method of avoiding photo-initiation by TMTM may be judged by the results given in Fig. 5. Curve I was determined on samples made up in ordinary room daylight with no precautions toward keeping light from the polymerization tubes at any time. Curve II gives the results when the solution of methyl methacrylate MMA–TMTM was made up in room light and then wrapped in aluminum foil after the polymerization tubes had been degassed and sealed off. Curve III shows the results when following the standard "dark" procedure. In the first two cases the line for conversion as a function of time does not pass through the origin, indicating that polymerization due to photoinitiation had been going on before the tubes were put in the thermostat bath. In the third case, however, the line hit the origin quite well indicating that photoinitiation was negligible.

Photoinitiation by TMTM.—As may be seen from Table VI, samples 1, 2 and Fig. 5, curve I, the splitting of TMTM into radicals by visible light is very rapid compared to the rate of thermal cleavage. A 0.1% solution of TMTM showed a conversion of 3.5% per hour in diffuse daylight at room temperature, while the thermal rate was two orders of magnitude lower than this.

TABLE VI

PHOTOINITIATION BY TMTM IN METHYL METHACRYLATE

Sample	(TMTM), mole/l.	Conditions	Rp, mole/l. sec.
1	4.80×10^{-3}	Diffuse daylight through soft glass room temp.	9.5×10^{-5}
2	4.80×10^{-3}	Dark, room temp.	5×10^{-7}
3	4.81×10^{-3}	Diffuse daylight room temp.	7.74×10^{-5}
4	4.66×10^{-3}[a]	Diffuse daylight room temp.	5.08×10^{-5}
5	4.81×10^{-3}	6″ from 60 watt bulb; room temp.	8.76×10^{-5}
6	4.66×10^{-3}[a]	6″ from 60 watt bulb; room temp.	4.68×10^{-5}
7	4.82×10^{-3}	0° in direct sun	9.2×10^{-5}

[a] Benzoin was the photoinitiator in these cases.

This high photo rate suggested a comparison of TMTM as a photoinitiator with benzoin which is used commercially in photo polymerization of vinyl monomers. The results shown in Table VI, samples 3, 4, 5, 6, demonstrate the somewhat greater activity of TMTM in this respect and especially its greater sensitivity to visible light from an incandescent filament. The greater sensitivity to visible light is to be expected since the absorption spectrum of TMTM shows a peak at about 400 mμ[14] which extends well into the visible region and gives TMTM its characteristic yellow color. This absorption corresponds to about 70 kcal./mole, and thus there is sufficient energy available from it to cleave the molecule at a C–S bond. Benzoin, on the other hand, gives white solutions indicating little absorption of light in the visible region. Sample 7 shows the high rate obtained at 0° by exposing the sample to sunlight. One calculates that at −40° the rate would still be 3.75×10^{-5} mole/l. sec. or 1.3% per hour.

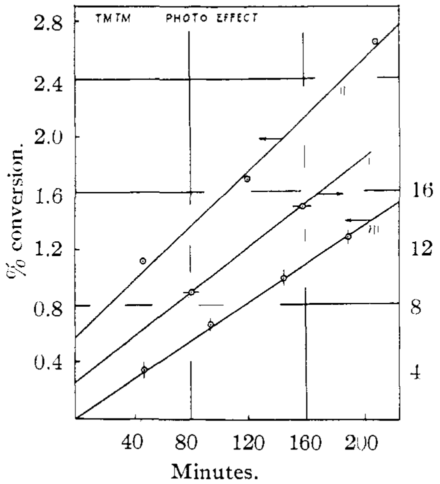

Fig. 5.—Test for thermal initiation by TMTM in methyl methacrylate: I, monomer and catalyst solution prepared and polymerized in the light, (TMTM) = 4.48×10^{-3} moles/l.; II, solutions prepared in light and polymerized shielded from light, (TMTM) = 4.48×10^{-3} moles/l.; III, solutions prepared and polymerized in the dark, (TMTM) = 4.76×10^{-3} moles/l.

Thermal Initiation of Polymerization by TMTM in Methyl Methacrylate.—The initiation of methyl methacrylate by thermal cleavage of TMTM was studied under the dark conditions described above. The data obtained are presented in Table VII and a sample plot of the data is given in Fig. 6. At each temperature separate runs were designed so that part of the same catalyst concentration range was covered. By this means any photo effect due, for example, to the light from the torch used in sealing off the tubes, should be detected since light conditions would not be precisely the same in the two different runs. No systematic variation was ever observed between runs, indicat-

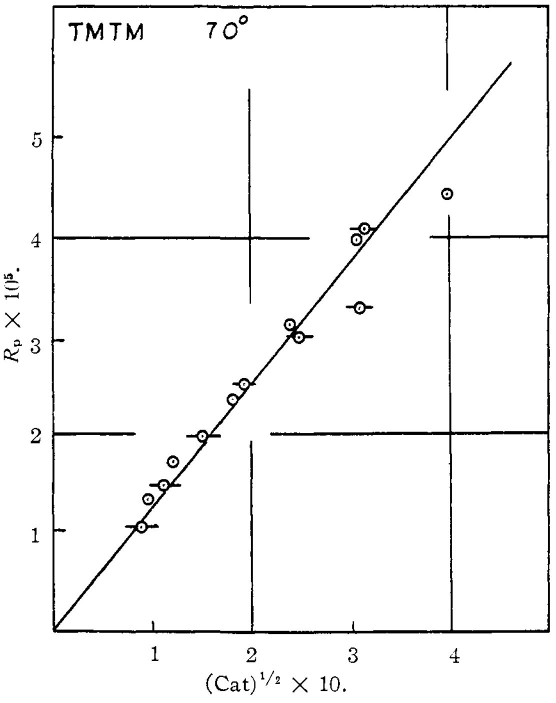

Fig. 6.—Polymerization of methyl methacrylate by TMTM at 70°: Run I, O; Run II, -O-.

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(14) H. Koch, *J. Chem. Soc.*, 403 (1949).

ing that the photo effect, if any, was not important. The two runs at 70° were, in fact, run at times four months apart yet the values checked each other very well. In each case a good line could be drawn through the points, although the scatter at 90° was a little larger than at lower temperatures. All of the values given are corrected for thermal polymerization as indicated under Table I.

TABLE VII

"THERMAL" INITIATION OF TMTM IN METHYL METHACRYLATE

A (70°)			B (80°)		
(cat.) × 10^{+2}, mole/l.	$R_p \times 10^5$	Run	(cat.) × 10^2, mole/l.	$R_p \times 10^5$	Run
0.786	1.06	b	0.340	1.41	c
0.836	1.33	a	.542	2.35	c
1.31	1.46	b	.926	2.93	c
1.39	1.72	a	.935	3.11	d
2.28	1.97	b	1.51	4.20	d
3.48	2.45	a	1.89	4.55	c
3.68	2.49	b	2.98	5.46	c
5.80	3.14	a	3.83	5.81	d
6.34	3.00	b	7.32	7.35	d
9.65	4.00	a			
10.0	4.11	b			
16.1	4.45	a			
		C (90°)			
0.225	2.78	e	1.05	5.73	e
.310	3.32	f	1.41	6.75	f
.345	3.62	e	1.58	5.65	e
.480	3.99	f	2.46	8.92	f
.566	5.29	e			
.800	5.79	f			

$R_{p,th}$, 70°, 0.5 × 10^{-5}; 80°, 0.98 × 10^{-5}; 90°, 1.21 × 10^{-5}.

It is interesting to note that there is no evidence for downward curvature of the plot of R_p^2 *vs.* (cat.) at higher catalyst concentrations such as is found with TMTD.

Assuming the usual radical kinetics, values of R'_i/(cat.) were calculated using equation 2 of reference 1 as in the case of TMTD. These results are presented in Table VIII.

TABLE VIII

RATE OF INITIATION OF METHYL METHACRYLATE BY TMTM

R'_i/(cat.), sec.$^{-1}$	T, °C.	A' (ref. 2)
1.91 × 10^{-8}	70	44
7.85	80	30.5
21.0	90	21.5

When an Arrhenius plot was made of the data a good straight line was obtained which fit the relation

$$\frac{R_i'}{(\text{cat.})} = 9.0 \times 10^{10} \exp\left(\frac{-29.4 \text{ kcal.}}{RT}\right) \quad (4)$$

The energy of activation for TMTM is quite close to that for TMTD (31.6 kcal.). The low frequency factor might possibly suggest that the thermal initiation of TMTM is due to unknown impurity, possibly TMTD.

Effect of Sulfur on TMTM Initiated Polymerization.—Vulcanization studies indicate that TMTM + Sg reacts the same in this reaction as TMTD. An exploratory run was made to note the effects of S_8 in polymerization by TMTM. A sample (9.3 × 10^{-3} mole/l TMTM + 11.7 × 10^{-3} mole/l. S_8) was polymerized at 80°. The observed R_p was 8.55 × 10^{-6}. The expected value for TMTM in the absence of sulfur was 2.39 × 10^{-5}. Thus there was some inhibition by sulfur under these conditions, rather than an acceleration.

Dipentamethylenethiuram Tetrasulfide (DPTT) Polymerization.—In view of the studies of Bartlett and Trifan[15] on the thermal polymerization of styrene in the presence of sulfur, a higher thiuram polysulfide was tested for activity toward vinyl monomers. The du Pont product "Tetrone A" was recrystallized from $CHCl_3$ to give light yellow crystals of DPTT melting at 115°. This pure product was studied in the polymerization of methyl methacrylate in the absence of light both alone and with TMTD. The results are given in Table IX. The tetrasulfide is seen to inhibit both thermal polymerization and that initiated by TMTD.

TABLE IX

ACTION OF DPTT ON METHYL METHACRYLATE AT 70°

(DPTT), mole/l.	(TMTD), mole/l.	R_p, mole/l. sec.
6.15 × 10^{-3}	....	1.79 × 10^{-6}
12.30 × 10^{-3}	....	1.87 × 10^{-6}
....	....	7.2 × 10^{-6}
6.15 × 10^{-3}	8.33 × 10^{-3}	2.24 × 10^{-5}
....	8.33 × 10^{-3}	6.93 × 10^{-5}

Diphenyl Disulfide.—The simpler compound diphenyl disulfide (Eastman white label) was recrystallized 3 times from hot benzene by H. Hsieh. It was found to have considerably lower initiating activity than TMTD or TMTM. However, one run was made at 100°. The results are given in Table X.

TABLE X

POLYMERIZATION OF METHYL METHACRYLATE BY DIPHENYL DISULFIDE AT 100°

(cat.), mole/l.	Conditions	R_p (cor. for thermal), mole/l. sec.
2.29 × 10^{-2}	Dark	7.87 × 10^{-5}
3.44	Light	12.35 × 10^{-5}
4.58	Dark	(−0.66 × 10^{-5})
5.73	Light	4.75 × 10^{-5}
6.86	Dark	(−0.85 × 10^{-5})

R_p, thermal = 2.56 × 10^{-5}.

There is some uncertainty in these figures since the thermal correction is so large compared to the total R_p. Also the dark conditions were not as stringent as usual since the run was carried out with aluminum foil wrapped tubes in a lighted room and some exposure to light during preparation of samples could not be avoided. Two conclusions, however, are certainly warranted. First, diphenyl disulfide shows photoinitiating activity and, second, it shows an initiating effect at low concentrations and a definite inhibiting effect on methyl methacrylate polymerization at higher concentrations. Two of the "dark" samples were even lower than the expected thermal rate. Both of these effects are less marked than for TMTD, but nevertheless quite similar.

Discussion

One of the initial purposes of these studies was to help in the understanding of the mechanism of the vulcanization of rubber by TMTD. Their greatest interest, however, has turned out to be the exploration of the complex features presented in the polymerization of vinyl monomers by compounds of the thiuram series. Of the thiuram compounds studied—the monosulfide—initiates polymerization, the disulfide both initiates and retards and the tetrasulfide retards only.

The initiation proceeds by a typical first-order cleavage of the initiator molecule. The relationship between R_p and (cat.) as well as molecular weight relationships for TMTD (see Part I) follow the pattern so thoroughly determined for polymerization by organic peroxides. Adding various polar reagents to the polymerizing system produces no appreciable change in the observed rate of polymerization. The rate of generation of radicals as determined by polymerization studies on the disulfide checks well with that estimated by use of the stable free radical diphenyl picryl hydrazyl (Part I).

Since the polymerization does proceed by a free radical mechanism, it is of interest to compare TMTD with the better known peroxide initiators as to bond strengths.

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[15] P. Bartlett and D. Trifan, *J. Polymer Sci.*, **20**, 457 (1956).

Cottrell's book[16] lists the following values for the bond dissociation energies of the various bonds of interest in the thiuram-sulfur compounds. The values for comparable bonds in peroxides are also included. These have been gathered in Table XI.

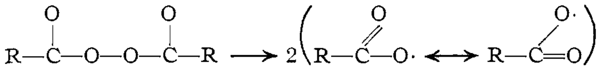
TABLE XI

BOND DISSOCIATION ENERGIES[16]

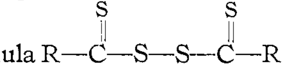
Bond	kcal.	Measured in
C–S	70	Lower alkyl monosulfides
C=S	120	CS_2
S–S	72	Et-S-S-Et
C–N	80	Methylamine
O–O	29	Acyl peroxides
O–O	35	Alkyl peroxides
C–O	90	Acetic acid
C=O	160	Ketones

Although these values were determined on simple molecules, they should at least give some indication of the relative magnitude of the strengths of the bonds involved.

From Table XI one notes that the peroxide O–O bond is considerably weaker than any of the others listed. Thus one can infer that peroxides will have the cleavage of this bond as the primary step in their decomposition. This corresponds to the results which were found experimentally. It also should be noted that the difference between alkyl and acyl peroxides is small even though the cleavage of the acyl peroxides leads to radicals with resonance stabilization.



$$\mathrm{R{-}\overset{O}{\overset{|}{C}}{-}O{-}O{-}\overset{O}{\overset{|}{C}}{-}R \longrightarrow 2\left(R{-}\overset{O}{\overset{/\!/}{C}}{-}O\cdot \longleftrightarrow R{-}\overset{O\cdot}{\overset{/}{C}}{=}O\right)}$$

Thus the 72 kcal. observed for the strength of the S–S bond in alkyl disulfides should give the order of magnitude of the S–S bond in compounds of the formula  $\mathrm{R{-}\overset{S}{\overset{\|}{C}}{-}S{-}S{-}\overset{S}{\overset{\|}{C}}{-}R}$, if these behaved analogously to the peroxides.

From these considerations one sees that the situation in organic disulfides is quite different from that in organic peroxides in that there is no one bond which is conspicuously weaker than all the others. The primary cleavage step for TMTD cannot be predicted from the bond dissociation energies which are currently available. Perhaps a small molecule such as CS_2 splits out in the primary cleavage.

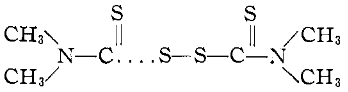
The study of TMTD in the presence of the initiator azobisisobutyronitrile in methyl methacrylate at 30° in the dark shows that the retarding effect of TMTD is not due to a species produced by spontaneous homolytic cleavage of the disulfide, rather it must be due to some stable substance which is present in the solution at all temperatures. The initiating species, on the other hand, does not appear at 30° until the solutions are exposed to visible light and sufficient energy is thus made available to split the molecule into radicals. These experiments suggest the picture that TMTD acts as a retarder by cleaving when attacked by a free radical so that the radical, which may be a growing polymer, becomes saturated by combining with one fragment of the TMTD. The other fragment which now has the radical activity is not polymerization active and eventually extinguishes another radical in the system. The initiating species is produced by cleavage at a different bond when sufficient energy is available from heat or light, the radicals produced in this mode of cleavage being active in initiating polymerization.

TMTM differs structurally from TMTD in that there is no S–S bond and no possibility of symmetric cleavage of the molecule. This compound also initiates the polymerization of methyl methacrylate, though it does not cleave thermally as readily as TMTD. The energy of activation for the over-all process of polymerization is very similar to that for the disulfide. The major difference in the behavior of the monosulfide from the disulfide is that no trace of retarding behavior is observed over a range of concentrations and experiments at three temperatures. The retarding action therefore must be connected with some radical species which is not readily available from TMTM.

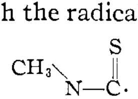
The studies of the tetrasulfide DPTT were more limited in extent, but in this case no indication of initiation was observed, only retardation. This compound then easily furnishes the retarding species.

Diphenyl disulfide also shows the mixed initiating and retarding behavior. The initiating action is different from that of the thiuram compounds in that it requires a higher temperature to activate it. The retarding action is more similar to those observed above.

These assembled observations give strong evidence that the retarding action of these sulfur compounds is associated with the breaking of the C–S bond, for example in TMTD as

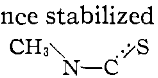


The disulfide radical generated here could not be formed from the monosulfide, but similar radicals could be formed from the tetrasulfide and diphenyl disulfide. Bloomfield[6] treated TMTD with dihydromyrcene and isolated two products one of which he attributes to a possible reaction of the dihydromyrcene with the radical

 IV

The other product apparently was formed by a complex route since it contained only C, H and S. Birch[13] also found evidence for inhibition by disulfide and higher radicals in acrylonitrile.

The mode of generation of the initiating species is not so clear cut. The most obvious picture for TMTD is a symmetrical cleavage at the S–S bond to give the resonance stabilized radicals

 I

This same radical could be formed from the monosulfide but would involve breaking at a C–S rather than an S–S bond. However, as noted above these two bonds are of comparable energy in simple compounds. The radical can then split off CS_2 so that

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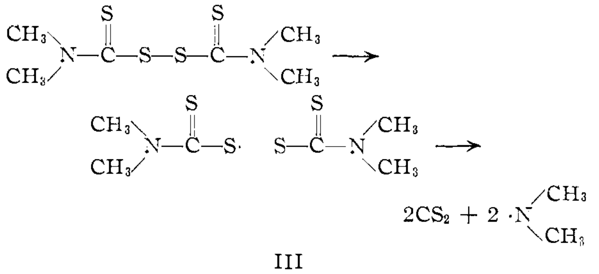
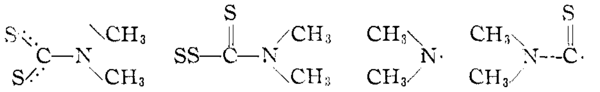
(16) T. L. Cottrell, "The Strength of Chemical Bonds," Academic Press, New York, N. Y., 1953.

an over-all reaction for generation of radicals is as given below.



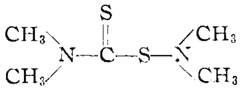
This picture has the advantage that it explains the pyrolysis products of TMTD. The radicals present due to the two possible modes of decomposition of TMTD are



I II III IV

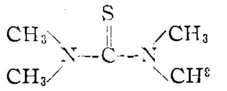
The observed pyrolysis products are[17]

CS_2 (major)



(minor)

and



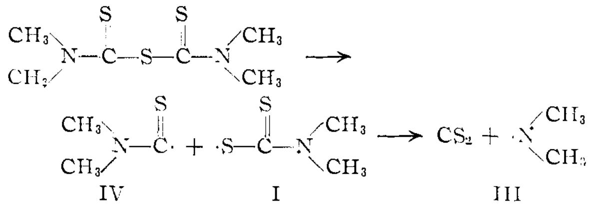
(major)

CS_2 is produced in the decomposition of intermediate I above.

The major product—tetramethylthiourea—is produced by the combination of radicals III and IV; the minor product by the combination of I + III or 2(III) + CS_2. The other possible combinations of these radicals would lead in general to regeneration of thiuram sulfides (mono, di, tri and tetra) and these would then go through the same sort of decomposition as described above. From the higher polysulfides one might expect to eventually get a trace of sulfur also, as has been observed.

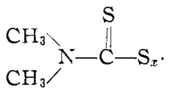
Koch[14] also has suggested a different complex mode of decomposition.

The behavior of TMTM also fits in the above picture. There is no possibility of forming radical II and this agrees with the fact that no inhibition is observed. Initiation can come about by a splitting at the C–S bond followed by splitting out of CS_2 in analogy with the above picture.



IV I III

The decomposition of the higher thiuram polysulfides would lead to the initiating radical but also to twice as many retarding radicals like II and a number of higher radicals which also would be expected to be retarders.[11]



$x_1 > 2$

Thus in these compounds the initiating activity might be concealed by the large retarding power.

In the case of diphenyl disulfide cleavage at the S–S bond would produce the radicals $C_6H_5S\cdot$ which would have initiating activity, while induced cleavage at a C–S bond would produce the inhibiting radical $C_6H_5SS\cdot$.

This mechanism for the decomposition of thiuram compounds cannot be regarded as proved. However, it is in accord with all the facts which have been obtained in this polymerization study with this class of compounds.

PRINCETON, NEW JERSEY

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[17] J. v. Braun and K. Weissbach, *Ber.*, **63**, 2836 (1930).

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY DIVISION, NATIONAL CHEMICAL LABORATORY]

Metal Protein Interactions in Buffer Solutions. Part II. A Polarographic Study of the Interaction of Zn^{II} and Cd^{II} with Bovine Serum Albumin

BY M. S. NARSINGA RAO[1] AND HIRA LAL

RECEIVED DECEMBER 2, 1957

It is concluded that binding data obtained from polarographic current ratios are comparable in accuracy with those obtained from equilibrium dialysis. A polarograpic study of competition between Zn^{II} and Cd^{II} for interaction with bovine albumin has been made: it is concluded that bovine albumin contains two sites, more reactive than imidazole, which combine with Zn^{II} in preference to Cd^{II}. It has been shown that the intrinsic constant for the interaction of Cd^{II} with bovine albumin, the two most reactive sites of which are covered by Zn^{II} ions, agrees well with the expected value for a 1:1 interaction with imidazole sites.

In Paper I,[2] we outlined general concepts governing the interpretation of binding data obtained in buffer solutions. Binding data themselves have been obtained by equilibrium dialysis and polarographic measurements. Whereas the major data for the binding of metal ions by bovine serum albumins have been obtained by equilibrium dialysis, we thought it worth while to investigate a selected few metal–bovine albumin systems polarographically, and to see if these measurements yield binding data comparable in accuracy to those obtained

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[1] Department of Chemistry, Clark University, Worcester 10, Mass.

[2] H. Lal and M. S. N. Rao, THIS JOURNAL, **79**, 3050 (1957).