K_d = dissociation constant of TlCl; $TlCl = Tl^+ + Cl^-$
K_2 = first dissociation constant of $TlCl_2^-$; $TlCl_2^- = TlCl + Cl^-$
S = solubility of thallous chloride, mole/liter

Values of $f_\pm$ given by Harned[11] for potassium chloride and sodium chloride solutions, and by Pearce and Pumplin[12] for ammonium chloride solutions, corrected for use with volume concentrations, were used to calculate (Tl^+).

Equation 2 shows that (TlCl) is constant at all concentrations of the added salt subject only to the condition that the activity coefficient of the neutral TlCl and the activity of the water are constant. Combining (3) and (4)

$$S - (Tl^+) = (TlCl) + \frac{(TlCl)}{K_2}(Cl^-)$$

We see that a plot of $S - (Tl^+)$ against (Cl^-) should give a straight line. The intercept at $(Cl^-) = 0$ is (TlCl); the slope is $(TlCl)/K_2$. K_d is given by equation 2.

From curves 1–3, Fig. 1, we see that such plots for the three solutions studied are nearly linear, at least in the concentration range where we expect (TlCl) to be really constant.

Similar analyses were made assuming that the value of q for the complex was greater than two. In these cases some uncertainty is introduced in choosing an appropriate activity coefficient for the multiply-charged complex ion; following the Debye–Hückel theory, f for such ions was taken as $Z^2 f_\pm$, where Z is the ionic charge and $f_\pm$, as before, is the mean value for the 1–1 electrolyte. If, for example, $TlCl_4^{---}$ is assumed to be present in addition to Tl^+ and TlCl, a plot of $S - (Tl^+)$ against $9f_\pm(Cl^-)^3$ should be linear; in reality such a plot shows very pronounced curvature over the entire concentration range, far exceeding any curvature which might have been introduced by an error in the assumed activity coefficient, and we must conclude $TlCl_4^{---}$ is definitely not the only negatively charged complex ion present. This was found true for other species of $q > 2$.

We consider now the possibility that ions of $q > 2$ are present in addition to $TlCl_2^-$. Then

$$S - (Tl^+) = (TlCl) + \frac{(TlCl)}{K_2}(Cl^-) + A(Cl^-)^2 + B(Cl^-)^3 + \ldots,$$

where $A, B \ldots$ are positive and involve (TlCl), dissociation constants, and activity coefficients. If $A, B, \ldots$ are not zero, there should be upward curvature in curves 1 to 3 of Fig. 1. This curvature is noted for KCl solutions at concentrations greater than about 2.5 *M*; however, it may be estimated from the curve that at 3 *M* the $TlCl_2^-$ concentration is at least 10 times that of complex ions of $q > 2$.

It is concluded that $TlCl_2^-$ is the only complex ion present in appreciable concentration, except in the KCl solutions of high concentration.

Further confirmation is provided by the use of an equation given by Reynolds and Argersinger,[13] modified to allow its use in solutions of high ionic strength

$$q = \frac{S_m C_m f_\pm^2}{S_m C_m f_\pm - K_s}$$

where S_m is the ionic concentration of thallous chloride at the point of minimum solubility, to include simple and complex ions but not neutral molecules such as TlCl, C_m is the chloride ion concentration at the minimum, and $f_\pm$ is the mean ionic activity coefficient for the thallium-containing ions. The equation is valid for the case in which only one complex ion exists in appreciable concentration, which is the case we have assumed initially. On the basis of the initial assumption, both the simple and complex ions of thallium are singly charged and thus $f_\pm$ for the added chloride is appropriate. The values of q calculated from the minimum points of the solubility curves are given in Table II; in all cases q was nearly 2, a value consistent with our assumption that $TlCl_2^-$ is the only negatively charged complex ion present in appreciable concentration in the range investigated.

TABLE II

DISSOCIATION CONSTANTS OF THALLOUS COMPLEXES AT 25°

Added salt	C_m, mole/l.	S_m, mole/l.	q	K_D	K_2
KCl	0.97	0.00096	2.2	0.26	1.7
NaCl	1.3	.00073	1.8	.26	2.3
NH_4Cl	1.3	.00075	1.9	.23	3.0
Av. for NaCl and NH_4Cl solutions				.25	2.7

The dissociation constants of TlCl and $TlCl_2^-$ are also given in Table II. Since the solid phase was not pure over the entire range of potassium chloride solutions, the dissociation constants so obtained were not included in the average. Onsager[10] reported 0.31, and Davies[14] 0.30, for K_D at 18°, in good agreement with our value, allowing for the temperature difference.

The pronounced discontinuity in the slope of the solubility curve in potassium chloride solutions at 3.5 *M* merits further investigation. We suppose it to be due to a change in composition of the solid phase with varying potassium concentration of the solution.

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[11] H. S. Harned, THIS JOURNAL, **51**, 416 (1929).

[12] J. N. Pearce and C. G. Pumplin, *ibid.*, **59**, 1219 (1937).

[13] C. A. Reynolds and W. S. Argersinger, *J. Phys. Chem.*, **46**, 417 (1952).

[14] C. W. Davies, *Trans. Faraday Soc.*, **23**, 354 (1927).

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Some Sulfur Compounds as Polymerization Sensitizers

BY R. J. KERN

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It has long been suspected that rubber chemicals operate *via* free radical mechanisms in vulcanization processes. A convenient tool for studying radical generation involves vinyl polymerization. This work reports the use of several sulfur containing rubber chemicals as polymerization sensitizers. Some sulfur-radical generating compounds have been so used before, diazothioethers as thermal[1] and disulfides as photo[2] sensitizers.

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[1] W. B. Reynolds and E. W. Cotten, *Ind. Eng. Chem.*, **42**, 1905 (1950).

[2] L. M. Richards, U. S. Patent 2,460,105 (1949).

TABLE I

CONVERSION AND VISCOSITY DATA

	Acrylonitrile Conv., %	Acrylonitrile Visc.^{a}	Meth-acrylonitrile Conv., %	Meth-acrylonitrile Visc.^{b}	Methyl acrylate Conv., %	Methyl acrylate Visc.^{b}	Methyl meth-acrylate Conv., %	Methyl meth-acrylate Visc.^{b}	Styrene Conv., %	Styrene Visc.^{c}	Vinyl acetate Conv., %	Vinyl acetate Visc.^{b}
						Thermal activation						
Tetramethylthiuram sulfide	8	0.085	13	0.25	1		25	0.13	38	0.06	0	
Tetramethylthiuram disulfide	10	.05	38	.03	17	0.04	38		80	.10	0	
Benzothiazolyl disulfide	4	.51	3	.19	15		1	0.13	37		0	
None	0		1	.32	^{e}		0		39	.18	0	
Time (hr.)	18		48		18		3		12		72	
						Photoactivation						
p-Thiocresol	11	1.87	6	0.01	Solid	0.46	2	0 014	13	0.11	59	0.14
2-Benzimidazolethiol	26	1.62	10	.36	Solid	0 40	34	.08	10	.19	12	.18
2-Benzoxazolethiol	19	1.46	8.5	.08	25	.35	12	.05	11	.07	1	
2-Benzothiazolethiol	7	0.45	7	.04	32	.055	8	.03	12	.03	0	
Tetramethylthiuram sulfide	34	0.17	55	.05	80	.06	47		28	.06	0	
None	0		5.5	.33	0		0		7	.20	0	
Time (hr.)	5^d		168^d		12		3		24		20	

^{a} 0.1% in dimethylformamide. 0.1% in acetone. ^{c} 0.1% in toluene. ^{d} In sunlight. ^{e} Cross linked gel.

Experimental

Materials.—All monomers were obtained from commercial sources and redistilled immediately before use. *p*-Thiocresol and 2-benzoxazolethiol were obtained from Eastman Kodak Co. All other sensitizers were obtained from the Monsanto Chemical Company and recrystallized from ethanol before use.

Procedure.—The monomer (15 cc.) and sensitizer (0.0004 mole) were sealed under nitrogen in a Pyrex tube. These tubes were wrapped to protect from light and then shaken until the sensitizer had dissolved. All dissolved completely except benzimidazolethiol which was not completely soluble in any of these monomers. Thermally activated polymerizations were carried out at 95° in a light-protected bath in which the tubes were not agitated.

Tubes being photoactivated were held in a circle six inches in diameter at the center of which was a General Electric B-H-4 100-watt bulb cooled by an electric fan.

After the indicated times tube contents were diluted or dissolved in benzene or acetone and precipitated in methanol. Precipitates were filtered, washed with methanol and dried. Vinyl acetate runs were precipitated in hexane while polyacrylonitrile was merely diluted and washed with methanol but not solvent purified.

Specific viscosities at 1 g. of polymer per liter of indicated solvent were determined at 25°.

Discussion

This work provides evidence that certain rubber chemicals give rise to free radicals in solution under thermal and photo activation. Very probably sulfur-type radicals are involved.

Noteworthy is the apparent specificity which some sensitizers show for certain monomers. This may signify varying free energies for sulfur-radical addition to monomer double bonds. In some instances apparent specificity may have resulted from a strong tendency to chain transfer with propagating radicals. Very low molecular weight material so formed would not have been recovered by the work-up procedure used, thus accounting for low conversions.

Times involved are quite significant. If the initial concentration of *p*-thiocresol in a photopolymerization of methyl methacrylate is not too great (0.05%), the bulk sample viscosity increases markedly some time after the start of irradiation. The observed effect is similar to an induction period during which an inhibitor is used up except that low molecular weight polymer is formed. *p*-Thiocresol may continue to function as photoinitiator after its concentration has become too low to be effective as a transfer agent.[3]

[3] The referee has suggested that the sulfur-containing product from *p*-thiocresol transfer cannot effect further transfer but can photosensitize.

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Anion-exchange Studies. XV. Separation of Protactinium and Iron by Anion-exchange in HCl–HF Solutions[1,2]

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It has been shown in previous papers that both Fe(III)[3] and Pa(V)[4] can be strongly adsorbed from relatively concentrated hydrochloric acid solutions by anion-exchange resins. Unfortunately the anion-exchange behavior of these elements is sufficiently similar that their separation with hydrochloric acid as eluant can be effected only by careful elution, as shown in Fig. 1 for a typical case.

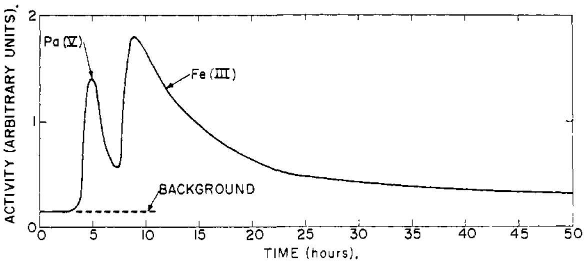

Fig. 1.—Separation of Fe(III) and Pa(V) by anion exchange with 3.8 *M* HCl (15 cm. column, flow rate 0.2–0.3 cm./min.).

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[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous paper: F. Nelson, THIS JOURNAL, **77**, 813 (1955).

[3] G. E. Moore and K. A. Kraus, *ibid.*, **72**, 5792 (1950).

[4] K. A. Kraus and G. E. Moore, *ibid.*, **72**, 4293 (1950).