TABLE I

CONVERSION AND VISCOSITY DATA

	Acrylonitrile		Meth-acrylonitrile		Methyl acrylate		Methyl meth-acrylate		Styrene		Vinyl acetate	
	Conv., %	Visc.^{a}	Conv., %	Visc.^{b}	Conv., %	Visc.^{b}	Conv., %	Visc.^{b}	Conv., %	Visc.^{c}	Conv., %	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]

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(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.

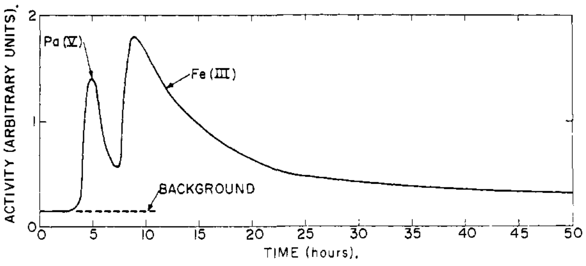

Fig. 1.—Separation of Fe(III) and Pa(V) by anion exchange with 3.8 *M* HCl (15 cm. column, flow rate 0.2–0.3 cm./min.).

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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).

Since it was found[5] that protactinium is only poorly adsorbed from HCl–HF mixtures at high HCl concentrations, it appeared of interest to investigate whether the separation of these two elements could be improved by the use of eluants consisting of HCl–HF mixtures.

In a series of column experiments with the same batch of a strong base polystyrene–divinylbenzene resin (Dowex-1) used in the earlier work, it was found that the adsorbability of Fe(III) from 9 *M* HCl solutions is not appreciably affected by addition of moderate amounts of hydrofluoric acid (*i.e.*, < 0.5 *M* HF). Hence, excellent separation of these two elements should be possible by the use of such mixed eluants. In Fig. 2 the results of a typical experiment are given in which both Pa(V) (Pa^{233} tracer) and Fe(III) (6 mg. of Fe with Fe^{59} tracer) were adsorbed from 9 *M* HCl on a 5 cm. × 0.12 cm.^{2} column. The Pa(V) was eluted with 9 *M* HCl–0.1 *M* HF. Under these conditions Fe(III) remained on the column. It was removed with 0.5 *M* HCl. The improvement over the separation described in Fig. 1 is apparent. Although elution was carried out in the HF–HCl experiment at high flow rates (*c*, 2.5 ml./cm.^{2}/min.), "tailing" of the iron band was very small and that of the protactinium band, though considerably larger, was still moderate. In the absence of HF extensive tailing is found (compare Figs. 1 and 2. Note that Fig. 1 gives concentration on a linear scale and Fig. 2 on a logarithmic scale).

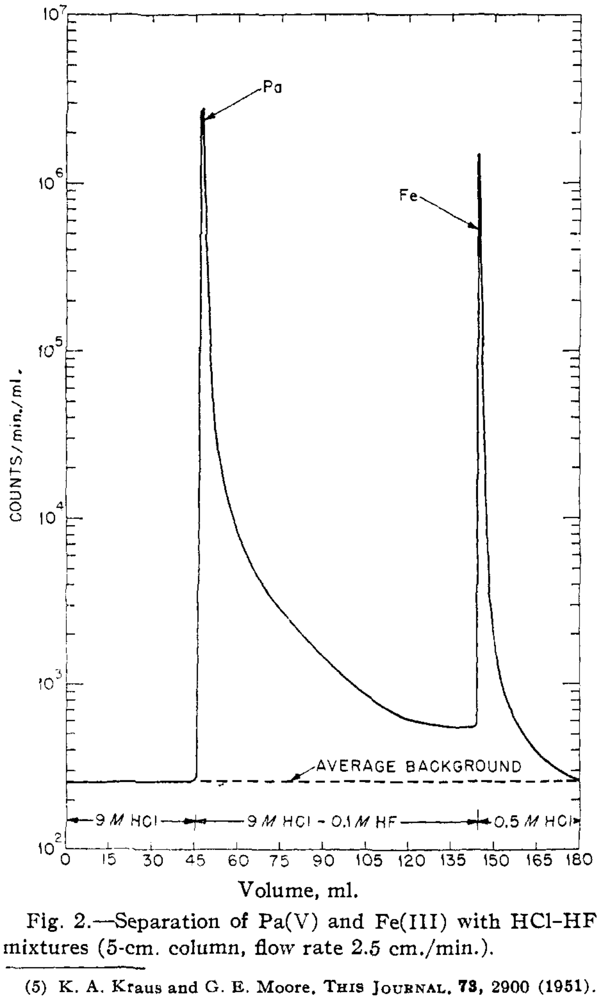

Fig. 2.—Separation of Pa(V) and Fe(III) with HCl–HF mixtures (5-cm. column, flow rate 2.5 cm./min.).

The pronounced difference in the effect of fluorides on the adsorbability of Pa and Fe indicates that protactinium forms a considerably stronger fluoride complex than iron. At considerably lower HCl concentrations where both elements are less strongly adsorbed in the absence of fluoride, fluoride complexing of iron may also become considerable, and the difference between the two elements may become less marked.

The procedure of complexing with two ligands (*e.g.*, chloride and fluoride) should be generally applicable for increasing the effectiveness of anion-exchange separations. Two elements often may show similar complexing properties with respect to one ligand, but it is less likely that they would also behave similarly with respect to two ligands. This property had earlier been taken advantage of in the separation of Nb, Ta and Pa.[5] It is now apparent that it may have general applicability and may be particularly useful in the separation of iron from other elements which show good adsorbability in chloride solutions and poor adsorption in HCl–HF mixtures such as Zr, Hf and Nb.[6]

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[5] K. A. Kraus and G. E. Moore, THIS JOURNAL, **73**, 2900 (1951).

[6] K. A. Kraus and G. E. Moore, *ibid.*, **73**, 9, 13 (1951).

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Metal-Amine Coördination Compounds. III.[1] Manganese Complexes with 2,2'-Bipyridine and 1,10-Phenanthroline

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The purpose of this investigation was to obtain further information concerning the nature and stability of the complexes formed by manganese(II) with 1,10-phenanthroline and 2,2'-bipyridine in solution.[2]

Experimental

Apparatus and Reagents.—Spectrophotometric curves were obtained with a Cary recording spectrophotometer. Individual absorption points were obtained with a Beckman Model B spectrophotometer. Matched 1-cm. cells were used with a distilled water blank.

The 2,2'-bipyridine and 1,10-phenanthroline were G. F. Smith Chemical Company reagent grade. The manganese(II) sulfate was obtained from Baker Chemical Company.

Spectrophotometric Study.—Neither the manganese 2,2'-bipyridine nor manganese 1,10-phenanthroline complex has an absorption maximum in the visible or near ultraviolet region of the spectrum as is shown in Fig. 1. In view of this, wave lengths of 370 and 395 mμ were arbitrarily taken to study the bipyridine and phenanthroline systems, respectively. These wave lengths were chosen for here the slope of the curve was not too great and yet the molar absorptivity was large enough so that the systems could be conveniently studied. It was found that the absorbance values of the manganese 2,2'-bipyridine and manganese

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[1] Previous paper in this series, W. W. Brandt and W. B. Howsman, Jr., THIS JOURNAL, **77**, 6319 (1955). Abstracted from a thesis submitted by Ronald R. Miller to the Graduate School of Purdue University, 1954, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Revs.*, **54**, 959 (1954).