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Radiosulfur-Exchange Reactions in Liquid Hydrogen Sulfide. I[1,2]

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Sulfur-35 has been used to study a number of solute–solvent exchange reactions in the solvent liquid hydrogen sulfide. In neutral solution the exchange rate is negligible or exceedingly slow with sulfur, carbon disulfide, dimethyl sulfide, or ethyl mercaptan. In basic, triethylamine-containing solutions, however, arsenic and antimony tri- and pentasulfides, carbon disulfide, and sulfur all show rapid exchange; phosphorus pentasulfide gives a moderate rate (apparently related to slow attainment of equilibrium among solute species), while ethyl mercaptan again shows no significant exchange. The results are interpreted as generally supporting the concept of the formation of thio anionic species in the basic solutions in those cases where moderate to fast exchange occurs.

Extending similar work with other nonaqueous solvents,[4] we have carried out some exploratory radiosulfur-exchange studies between the solvent liquid hydrogen sulfide and a variety of solutes. The solvent properties of this relatively low dielectric constant medium (8.04 at $-61.2°$[5]) have been reviewed by Wilkinson[6] and Jander.[7] Among other phenomena, Jander describes the amphoterism of arsenic trisulfide; the material, insoluble in neutral solution, reportedly dissolving on addition of either hydrogen chloride or triethylamine. The basic solution is presumed to contain thioarsenite, formed by reaction with $((C_2H_5)_3NH)SH$[8,9]

$$As_2S_3 + 6((C_2H_5)_3NH)SH = 2((C_2H_5)_3NH)_3AsS_3 + 3H_2S \quad (1)$$

If reactions of type 1 occur, arsenic trisulfide and related materials should, on being dissolved and later recovered from triethylamine-containing solutions, show at least partial sulfur exchange with the solvent (rapid exchange between $((C_2H_5)_3NH)SH$ and solvent being assumed). Depending on the rate of solvent–thio anion exchange, the net observed exchange might or might not be complete. Analogous isotopic oxygen exchanges between oxy anions and water have been found very slow in some cases and in others relatively rapid.[10] In view of the interest of this matter, exchange experiments with various possible thio anion forming solutes have had a central place in the present work.

Experimental Section

Preliminary Observations.—Very little solubility in neutral hydrogen sulfide was found for the group V sulfides here studied (estimated <0.05 g/100 g of solvent for As(III), Sb(III), or P(V)) and only moderate solubility for elemental sulfur (estimated ~0.4 g/100 g, colorless solution), observations generally consistent with prior reports[11] (though conflicting with one[12]). On the other hand, in harmony with the concept of thio anion or (for sulfur) polysulfide formation, all of these materials were readily soluble in triethylamine-containing solvent, giving colored solutions (As_2S_3, yellow, As_2S_5 and Sb_2S_3 greenish yellow, Sb_2S_5 brownish orange, P_4S_{10} yellow, fading with time, S_8 yellow to deep red). For arsenic trisulfide, for example, a 4.6:1 amine–As_2S_3 mole ratio more than sufficed to dissolve 0.08 *m* As_2S_3 (less, incidentally, than the 6:1 ratio required by eq 1, taken from Jander;[7] thio anion formation, while suggested, is evidently not limited to the process depicted by (1)). In the case of sulfur, solubility in a 2.2 *m* amine solution amounted to at least 2.8 g-atoms/mole of amine.

Solvent evaporation *in vacuo* from the basic solutions leaves decomposable solid residues differing in appearance from the original solutes and showing variable retentions of amine and excess sulfur (approximately up to amounts, for group V species, corresponding to ortho thio anions). It may be noted, incidentally, that hydrogen sulfide solutions of triethylamine alone also leave a residue (white, $((C_2H_5)_3NH)SH$?); a material, however, readily decomposing in the evaporative separations used in this work. Sulfur solutions leave a red-orange solid of indefinite composition, which appears to decompose to a sulfur residue corresponding at least roughly to that originally present in about 2 days in air at room temperature. The red residue is decomposed by water or acetone but appears to dissolve somewhat in benzene, ether, or carbon tetrachloride without decomposition. One quantitative experiment suggested for this material the approximate composition of a five-sulfur polysulfide.

Carbon disulfide, ethyl mercaptan, and dimethyl sulfide were readily miscible with hydrogen sulfide to give colorless solutions. Addition of triethylamine, though giving no color with mercaptan, produced yellow to red-orange solutions with carbon disulfide, suggestive of thiocarbonate formation.

Materials.—Hydrogen sulfide from a cylinder was, following Bickford and Wilkinson,[13] passed successively through two saturated barium hydroxide solutions (at 0°), a $-20°$ trap, calcium chloride, phosphorus pentoxide, and then, condensed as liquid in a Dry Ice trap, fractionated *in vacuo*, the middle third

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[3] Taken from the Ph.D. Thesis of J. R. Mickelsen and the M.S. Thesis of R. C. Smith, Oregon State University, June 1956 and June 1952.

[4] *Cf.* R. R. Wiggle and T. H. Norris, *Inorg. Chem.*, **3**, 539 (1964).

[5] S. Havriliak, R. W. Swenson, and R. H. Cole, *J. Chem. Phys.*, **23**, 134 (1955).

[6] J. A. Wilkinson, *Chem. Rev.*, **8**, 237 (1931).

[7] G. Jander, "Die Chemie in Wasserähnlichen Lösungsmitteln," Springer-Verlag, Berlin, 1949, pp 77–119.

[8] Jander's visualization of triethylamine in liquid hydrogen sulfide as $((C_2H_5)_3NH)SH$ dates from a time when analogous aqueous hydroxide species were commonly so written. Although present knowledge indicates the actual dominance in water systems of the free amine bases, it does seem possible, in view of the relative stability of amine hydrosulfides,[9] that a substantial conversion of amine to a hydrosulfide (ion paired) may occur in the present medium. The validity of this assumption, however, is not especially material to the interpretation of the present results.

[9] M. Achterhof, R. F. Conaway, and C. E. Boord, *J. Am. Chem. Soc.*, **53**, 2682 (1931).

[10] (a) A. I. Brodskiĭ and L. V. Sulima, *Dokl. Akad. Nauk SSSR*, **92**, 589 (1953); (b) N. F. Hall and O. R. Alexander, *J. Am. Chem. Soc.*, **62**, 3455 (1940).

[11] "Gmelins Handbuch der Anorganischen Chemie," Vol. B-1, 8th ed, System No. 9, Verlag Chemie, Weinheim/Bergstrasse, 1953, pp 115–117.

[12] G. N. Quam, *J. Am. Chem. Soc.*, **47**, 103 (1925).

[13] W. G. Bickford and J. A. Wilkinson, *Inorg. Syn.*, **1**, 111 (1939).

being retained. Triethylamine and dimethyl sulfide, stored over sodium, were dried before use over fresh sodium and fractionated *in vacuo,* the middle third being taken. Phosphorus pentasulfide and sulfur were recrystallized from carbon disulfide and dried at 110 and 40°, respectively. Arsenic and antimony trisulfides and antimony pentasulfide were washed successively with hydrochloric acid ($\sim 1\ M$, saturated with hydrogen sulfide), alcohol, carbon disulfide, alcohol, and hydrochloric acid ($\sim 1\ M$) and were finally dried *in vacuo* over phosphorus pentoxide. Carbon disulfide and ethyl mercaptan were dried *in vacuo* over phosphorus pentoxide, then fractionated, the middle third being retained.

Arsenic pentasulfide was prepared[14] by dissolving the pentoxide in base, treating with chlorine, acidifying, and precipitating with hydrogen sulfide from concentrated hydrochloric acid solution. The preparation, washed with acid, water, alcohol, carbon disulfide, and alcohol, was dried *in vacuo* over calcium chloride. Some work involved material dissolved in and reprecipitated with acid from sodium polysulfide (sulfur eliminated by thorough washing with carbon disulfide). Either preparation appeared to give comparable results.

Labeled Materials.—Sulfur-35 was obtained from the Oak Ridge National Laboratory as elemental sulfur in benzene solution. Labeled experimental sulfur was prepared by dilution of the high specific activity material (after benzene evaporation) with inactive sulfur in carbon disulfide. Portions of this solution were evaporated as needed. Labeled hydrogen sulfide was prepared *via* the rapid exchange found with elemental radiosulfur dissolved in liquid hydrogen sulfide containing triethylamine (needed both to promote solubility and catalyze exchange). After brief contact, the active hydrogen sulfide was distilled off (through phosphorus pentoxide to remove amine) and stored as gas.

Labeled carbon disulfide was prepared by the heterogeneous exchange[15] occurring on shaking inactive carbon disulfide for 24 hr with labeled aqueous sodium sulfide (activated by dissolving a little active sulfur). Separated with a pipet, the preparation was dried *in vacuo* over phosphorus pentoxide and fractionated, the middle half being retained. Tests with labeled hydrogen sulfide and inactive carbon disulfide showed the adequacy of the fractionation for eliminating any active hydrogen sulfide contamination generated by reaction between drying agent and any transferred traces of aqueous sulfide.

Exchange Procedure.—Standard high-vacuum procedures were used, similar to those previously described.[4] Exchange experiments were done in 6-mm o.d. sealed Pyrex tubes, ordinary tubing sufficing despite pressures of *ca.* 20 atm at 25°. Volatile reactants were dosed from calibrated volumes as gas or liquid. Sulfur was introduced by evaporation of measured volumes of carbon disulfide solutions. Other solids were weighed out. The experiments were commenced by bringing the solute and solvent (one labeled) together and effecting solution at the chosen run temperatures. (Four "preequilibrated" phosphorus pentasulfide experiments, described below, represented a deviation from this procedure.) Temperatures of the exchange bombs were maintained by appropriate liquid baths. Except as noted, the reactants were separated by evaporation of the solvent *in vacuo,* the solution being held at Dry Ice temperature.

In the sulfur and carbon disulfide–triethylamine experiments, the solute was initially labeled; otherwise the solvent was labeled. For radioassay, samples were converted to barium sulfate and counted on planchets under an end-window GM tube, all appropriate corrections being applied. The fraction exchange was determined as the ratio of the final observed specific activity of the initially inactive fraction, divided by that expected for complete exchange, usually calculated either on the basis of complete randomization of the known initial activity or from the measured total activity in the two separated solute and solvent fractions. In some cases the complete exchange specific activity was also checked directly by infinite time experiments.

Exchange with Group V Sulfides.—Experiments were done in triethylamine-containing solutions. Final separations involved solvent evaporation, followed by warming of the residue with a tepid water bath, both *in vacuo.* This procedure left the residue with varying amounts of retained sulfur in excess of that originally present, any compound formed in the solution presumably having been only partially (and to a variable extent) decomposed. The residue was oxidized by fusion with sodium peroxide, and barium sulfate was precipitated for counting from an aqueous solution of the resulting oxidized material. The fraction exchange was calculated from the specific activity of this group V fraction *as recovered* and as compared to the complete exchange value expected from the original solvent activity. The retention of varying amounts of excess sulfur by the residues meant that at least a corresponding degree of apparent zero time exchange was of necessity to be expected in these experiments. To meet this difficulty alternative fraction exchange calculations were also made on the basis of recovered solute specific activities corrected for retained excess sulfur, the latter being assumed to have the specific activity of the solvent. While, relative to values one might expect for fully desolvated solute, the uncorrected fraction exchanges would err, if at all, on the high side, any error in the corrected values would be on the low side.

In the four supplemental phosphorus pentasulfide experiments, done to permit solution equilibration prior to exchange, solutions were prepared with inactive solvent at 2.5 times the concentration in the other, "nonequilibrated" experiments. After 2–6 days at room temperature, labeled solvent was added in sufficient amount to match the "nonequilibrated" concentration. After short times, separation and counting were then carried through as in the other cases.

Elemental Sulfur Exchange.—Experiments in both neutral and basic solution were done essentially the same way. At the end of the run the solvent was distilled off from the initially active sulfur, onto frozen copper nitrate solution, in which, after thawing occurred, copper sulfide precipitated. This precipitate and the recovered sulfur residue, the latter with excess carrier added, were, for radioassay, each oxidized to sulfate by sodium peroxide fusion. Because of the use of excess carrier, any solvent sulfur retention by the residues in the amine experiments had no important effect on the calculated exchange results.

Carbon Disulfide Exchange.—The neutral solution runs were terminated by distilling off the bulk of the solvent. The residue, largely carbon disulfide (initially inactive), was converted to xanthate by reaction with alcoholic potassium hydroxide, and this material was then oxidized to sulfate with sodium peroxide in basic solution for counting and fraction-exchange determination. In runs with amine, solute being initially labeled, a small portion of the solvent was evaporated, absorbed in copper nitrate, and converted to barium sulfate for fraction-exchange determination.

Ethyl Mercaptan Exchange.—Both neutral and basic solution runs were terminated by distilling the reactants *in toto* into copper nitrate. The precipitated sulfide and mercaptide were oxidized with bromine and nitric acid to sulfate and sulfonate, respectively, the former then being precipitated as barium sulfate. The sulfonate filtrate was evaporated, and the residue was oxidized to sulfate by sodium peroxide fusion, this then being precipitated for determination of percentage exchange.

Dimethyl Sulfide Exchange.—At the end of the single, neutral solution experiment, the solvent was distilled off until the residue amounted to only about half the original solute volume. This fraction was ignited with a torch under an inverted funnel through which an air stream was drawn. The fumes were drawn through base to collect sulfur dioxide, which was then oxidized, precipitated, and counted.

Results

Elemental Sulfur Exchange.—The results of studies of the exchange between dissolved elemental sulfur and

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[14] W. W. Scott, "Standard Methods of Chemical Analysis," Vol. 1, N. H. Furman, Ed., 5th ed, D. Van Nostrand Co., Inc., New York, N. Y., 1939, p 95.

[15] R. R. Edwards, F. B. Nesbett, and A. K. Solomon, *J. Am. Chem. Soc.,* **70**, 1670 (1948).

the solvent in neutral and basic triethylamine-containing solutions are summarized in Tables I and II.

TABLE I

RADIOSULFUR EXCHANGE IN NEUTRAL HYDROGEN SULFIDE

Solute[a]	Temp, °C	Reaction times,[d] hr	No. of expts	Exch, %	Estd $t_{1/2}$, years
S_8[b]	25	21–5110	11	4.5 ± 3.3[e]	4 ± 2[g]
S_8[b]	0	622–4336	6	3.9 ± 2.5[e]	>9[h]
CS_2[c]	25	2.5–1224	4	0.8 ± 0.7[e]	>6[h]
C_2H_5SH[c]	25	14–384	2	2.0 ± 0.6[e]	>1[h]
$(CH_3)_2S$[c]	20	144	1	0 ± 0.5[f]	>2[h]

[a] Concentrations: S_8, 0.012 or 0.015 *m*; C_2H_5SH, 6.9 *m*; $(CH_3)_2S$, 9.3 *m*; CS_2, 1.32 *m*. [b] Sulfur initially labeled. [c] Solvent initially labeled. [d] Durations of individual experiments were distributed over indicated range of times; no evident trend with time except possibly for sulfur at 25°. [e] Averages and experimental standard deviations of individual experiments. [f] Uncertainty based on estimated uncertainty of counting data. [g] From least-squares McKay plot. [h] Maximum McKay slope based on estimated exchange uncertainties.

TABLE II

RADIOSULFUR EXCHANGE IN TRIETHYLAMINE-CONTAINING HYDROGEN SULFIDE

Solute	Temp, °C	Reaction times,[h] min	No. of expts	Exch,[j] %	Estd $t_{1/2}$,[n] min
S_8[a,e]	25	10–90	11	96 ± 3	<3
S_8[a,e]	5	15–90	3	97 ± 0	<4
S_8[a,e]	−26[g]	~2	2	96 ± 1	<1
S_8[a,e]	−78	1400	2	97 ± 0[k]	
As_2S_3[b,f]	25	2–11	5	94 ± 7[l]	<1
As_2S_3[b,f]	0	15	1	~108[l]	<3
As_2S_3[b,f]	−78	10–30	3	100 ± 8[l]	<4
As_2S_5[b,f]	25	5, 60	2	94 ± 19[l]	<3
As_2S_5[b,f]	0	5–30	4	97 ± 6[l]	<1
Sb_2S_3[b,f]	0	5–15	3	96 ± 4[l]	<2
Sb_2S_5[b,f]	0	5, 15	2	91 ± 0[l]	<2
CS_2[c,e]	25	5–50	2 (5[i])	101 ± 8	<2
C_2H_5SH[d,f]	25	8640	1	3 ± 2[m]	$>1 \times 10^5$

[a] Range of concentrations: S_8, 0.012–0.023 *m*; $(C_2H_5)_3N$, ~10^{-8}–2 *m* (25°) or 0.51–0.78 *m* (other temperatures). [b] Range of concentrations: sulfides, 0.05–0.08 *m*; $(C_2H_5)_3N$, 0.4–1.5 *m*. [c] Concentrations: CS_2, 1.32 *m*; $(C_2H_5)_3N$, 0.182 or 0.94 *m*. [d] Concentrations: C_2H_5SH, 6.9 *m*; $(C_2H_5)_3N$, 0.15 *m*. [e] Solute initially labeled. [f] Solvent initially labeled. [g] About 2-min dissolving time at −26° was followed by 15 and 45 min, respectively, at −78°. [h] Durations of individual experiments were distributed over indicated range of times; trends with time absent or indefinite. [i] Number of successive samples taken from two individual experiments; times, exchange average, and standard deviation refer to total samples. [j] Averages and experimental standard deviations of individual experiments or samples. [k] Samples at 700 min showed 85 ± 4% exchange. [l] Calculations based on recovered solute specific activities without correction for excess retained sulfur; over-all average, all arsenic and antimony sulfides: 96 ± 8%. Over-all average, same experiments, corrected for excess retained sulfur (assumed of equal specific activity with solvent): 94 ± 8%. Average exchange (uncorrected) expected on basis of same excess retained sulfur alone: 35 ± 16%. Average total recovered sulfur, per g-atom of original sulfur: As(III), 1.54 ± 0.26; As(V), 1.66 ± 0.35; Sb(III), 2.15 ± 0.38; Sb(V), 1.08 ± 0.02. [m] Uncertainty based on estimated uncertainty of counting data. [n] Minimum or maximum McKay slopes based on estimated exchange uncertainties.

The neutral solution experiments, lasting up to 0.5 year or more, showed no significant exchange rate either at 0 or 25°, the recorded small apparent exchanges presumably representing mainly separation errors. Least-squares McKay plots of the data have been made in an effort to obtain an indication either of the general magnitude of any possible actual rate or at least of the minimum value of any such rate. While the scatter is considerable, the 25° data do suggest an actual rate (t test indicates 92% confidence level), with the recorded half-time of 4 ± 2 years. At 0°, no such progressing exchange is apparent, the indicated McKay rate being indistinguishable from zero and the estimated minimum half-time being at least the recorded 9 years. Although the 25° estimate may or may not be quantitatively valid, the experiments clearly show the exchange rate to be at best exceedingly slow.

Triethylamine-containing solutions provided a complete contrast to the exchange-inert neutral solutions. Here the exchange of elemental sulfur with the solvent was fast and essentially complete even at −26° and remained at least quite rapid at −78°. (As indicated in Table II, there was some suggestion of a measurable rate at −78°; attempted short-time experiments at this temperature were, however, invalidated by the probable incomplete dissolving of sulfur.) At 25° experiments were carried to quite low amine concentrations in an effort to find a measurable rate. While the lowest indicated concentration can be considered only an approximation, it is clear that an extremely modest amine concentration sufficed to yield complete exchange within the time of these experiments. Maximum estimated exchange half-times presented in Table II represent conservative figures based on estimated limits of error in the observed apparent exchanges in the shorter time (and low amine concentration) experiments.

Arsenic and Antimony Sulfides.—The results of exchange experiments between arsenic and antimony tri- and pentasulfides and the solvent in basic triethylamine-containing solutions are recorded in Table II. (Low solubilities prevented neutral solution experiments.) The tabulated figures indicate rapid and substantially complete exchange in every case, even, where studied, at −78°. Exchange in these experiments was assessed on the basis of the specific activities of recovered but only partially desolvated solute sulfides (pure, inactive sulfides having been the starting materials), the average excess sulfur retention varying, as indicated in Table II, from ~0.08 to ~1.15 g-atoms/g-atom of original sulfur. In view of the completeness of the exchanges, excess retained sulfur was without important effect on the calculated results; exchanges computed from solute activities corrected for the excess sulfur (assumed to have the solvent specific activity) came out only about two percentage points lower on the average. An alternative demonstration of the unimportance of sulfur retention relative to the exchange calculation is furnished by the average apparent exchange (uncorrected) of only 35% which this retained sulfur alone (no further exchange occurring) would have yielded. Clearly the solute–solvent exchange, quite apart from excess retained sulfur, was rapid and essentially complete in all cases. The indi-

Table III

Phosphorus Pentasulfide–Hydrogen Sulfide Exchange[a]

Temp, °C	Reaction times, min	No. of expts	$(100)F_0$,[b] %, uncor[d]	$(100)F_0$,[b] %, cor[d]	$t_{1/2}$, min,[b] uncor[c]	$t_{1/2}$, min[b] cor[d]
25	2–90	12	28 ± 4	13 ± 7	44 ± 3	41 ± 5
14.5	15–480	11	41 ± 7	21 ± 7	222 ± 32	214 ± 26
−15	15–1440	5	41 ± 7[f]	27 ± 4[f]	$>4 \times 10^3$[g]	$>8 \times 10^3$[g]
−78	45–5760	6	30 ± 12[f]	20 ± 9[f]	$>1 \times 10^4$[g]	$>8 \times 10^4$[g]
25[e]	2–20	4	73 ± 15	76 ± 32	10 ± 3	20 ± 21

[a] Concentrations: P_4S_{10}, 0.045 *m*; $(C_2H_5)_3N$, 0.60 *m*. Solvent initially labeled. [b] Values and standard deviations from least-squares McKay plots. [c] Calculations based on recovered solute specific activities without correction for excess retained sulfur. Over-all average zero time exchange (uncorrected) expected on basis of excess retained sulfur alone (assumed of equal specific activity with solvent): 20 ± 9%. Over-all average total recovered sulfur, per g-atom of original sulfur: 1.26 ± 0.19. [d] Calculations based on corrected specific activities of recovered solutes, excess recovered sulfur and solvent specific activities assumed equal. [e] Two to six days pre-equilibration of solute in inactive solution before beginning of exchange. [f] Averages and experimental standard deviations of apparent exchanges spread over indicated time ranges. No obvious trends with time. Least-squares intercepts almost the same. [g] Values based on observed apparent least-squares McKay slopes: $(4.0 \pm 4.2) \times 10^{-5}$ min^{-1} (−15°, uncor); $(1.6 \pm 2.3) \times 10^{-5}$ min^{-1} (−15°, cor); $(7.4 \pm 15.4) \times 10^{-6}$ min^{-1} (−78°, uncor); $-(6.7 \pm 10.6) \times 10^{-6}$ min^{-1} (−78°, cor).

cated approximate maximum half-times represent conservative values based on estimated lower limits for the percentage exchange in the shorter time experiments.

Phosphorus Pentasulfide Exchange.—The exchange of phosphorus pentasulfide with the solvent was studied in triethylamine-containing solutions; low solubility again prevented neutral solution experiments. As with the other group V sulfides, the extent of the reaction was assessed from the specific activities of the only partially desolvated recovered solutes. Hence, the exchange has again been calculated both on the basis of the raw, uncorrected recovered solute activities and also on the basis of solute activities corrected for excess retained sulfur, assumed of equal specific activity with the solvent. As indicated in the Experimentale Sction, the figures so obtained should bracket the "true" value to be expected for a fully desolvated solute.

The results (Table III) differ from those observed with the other group V sulfides in showing only moderate zero time exchanges, followed, at the two higher temperatures, by apparently progressing exchanges of conveniently measurable rates. The experiments at the latter temperatures, spread over the indicated time ranges, gave, though with some scatter, reasonably satisfactory McKay plots (both corrected and uncorrected data) leading to the recorded half-times and zero time exchanges. An additional experiment at 25° showed 96.5% exchange in 1260 min, essentially complete within experimental error. The apparent half-times, quite similar for either corrected or uncorrected data, suggest an activation energy (latter data) of about 26 kcal/mole. At the two lower temperatures the apparent rates were not clearly distinguishable from zero, McKay plots providing the estimates of minimum half-times.

The zero time exchanges shown by the uncorrected data are, naturally, higher than for the corrected data. The significant values of the latter, however, clearly demonstrate a real effect. Weighted averages of the apparent zero time exchanges for all four temperatures (excluding the "equilibrated" experiments, discussed below) are 34% (uncorrected) and 19% (corrected). A "true" figure, which would apply to a fully desolvated solute, should lie between these figures and probably not too near either extreme.

Besides the apparently lower exchange rates, an important difference shown by the present solutions as compared to the other group V sulfides is the observation that the initial color of the solutions tends to fade with time. Such an effect implies that the first formed solutions are not at equilibrium and that an initial solute species may slowly be transformed to one or more other species. Clearly, such a situation complicates the interpretation of the exchange observations. The question may be asked, for example, whether the apparent exchange rates, despite their seeming conformance to conventional McKay plots, may actually correspond to the rates of such solute-transformation processes. Might the initial species have only a slow inherent exchange rate and the later-formed species exchange much faster? Pertinent here is the observation that the apparent exchange rates appear roughly to be paralleled by the rates of color fading, none of the latter being evident at the two lower temperatures.

In view of the foregoing considerations, further exploratory experiments were done at 25° in which chemical equilibrium should have been established prior to exchange. After 2–6 days equilibration with inactive materials, labeled solvent was mixed with the solutions, and then, over short periods, the experiments were completed as before. A McKay plot of the data gave the results shown on the last line of Table III, the apparent zero time exchange now having the much enhanced value, compared to the previous data, of 73–76% and the exchange half-time having the smaller value of 10–20 min. These results support the general postulate of more rapidly exchanging solute material in the equilibrium solution. Yet they also invite further study. The large zero time exchange coupled with a measurable rate is interesting, for example, since, with initially inactive solvent, one might have anticipated a negligible initial exchange (in contrast to the situation with solvent initially labeled). A possible explanation might involve an equilibrium solute species with non-exchange-equivalent sulfurs. Alternatively (consistent with the observation that color never completely disappeared from the solutions), perhaps the equilibrium solutions may contain more than one species, the principal one exchanging very rapidly to give the observed large zero time effect and a second exchanging more slowly. The limited nature of the present data, however, suggest that further speculation should await more extensive studies.

Carbon Disulfide Exchange.—Exchange with the solvent was studied both in neutral and basic solutions. The results (Tables I and II) present a close parallel to those obtained with sulfur or (in basic solution) with arsenic and antimony sulfides. Neutral solutions showed no significant solute–solvent exchange rate. On the other hand, in basic solution the exchange (at 25°) was rapid and complete. It must be noted, however, that for the basic solutions the parallel is not quite complete, in that, in experiments at lower temperatures, it has been possible to observe measurable rates and to study the exchange kinetics. These results, interpreted in terms of thiocarbonate formation in the solutions, form the subject of a subsequent publication.[16]

Ethyl Mercaptan and Dimethyl Sulfide Exchange.—The exchange of dimethyl sulfide with the solvent was investigated in neutral solution, and that of ethyl mercaptan was investigated in both neutral and basic solution. The results (Tables I and II) indicate the absence of any significant exchange rate in any of the three cases.

Discussion

Experiments in Neutral Solution.—In general consistency with expectations, the low dielectric constant medium appears to show a bias toward solvent action for covalent materials, but there seems little tendency toward solute–solvent exchange interaction. The almost negligible exchange rate shown by elemental sulfur, for example, illustrates this point, the sulfur presumably being present in the inert solvent, as in other low-polarity media, as S_8 rings (a feature which would be interesting to check spectrophotometrically). Such a result is consistent with the very slow radiosulfur-exchange rates observed in other such media, *e.g.*, sulfur in sulfur monochloride,[17] sulfur and sulfur monochloride in carbon tetrachloride[18] or ethylene dibromide,[19] or sulfur in carbon disulfide.[20] The results with carbon disulfide solute similarly imply the absence of any important interaction with solvent, such as might be involved, for example, in thiocarbonic acid formation in the solution. This result serves to complement the earlier observation of lack of sulfur exchange, even at 120°, between these same reactants in benzene solution.[21]

The dimethyl sulfide and ethyl mercaptan experiments illustrate further situations where stably bonded sulfur would not be expected to exchange. The result with mercaptan, one may note, finds its analogy in the nonexchange of oxygen between methanol and water.[22] In this connection, it further may be noted that, just as in water, methanol in liquid hydrogen sulfide does give rapid hydrogen exchange.[23]

Experiments in Triethylamine-Containing Solutions.—The exchange rates in basic, triethylamine-containing solutions contrast sharply with those in neutral solution.

These experiments were designed mainly to provide evidence for or against the concept of thio anion formation in basic solution. No rapid solute–solvent exchange, for example, would have been expected to ensue from a solution process for group V sulfides involving only an interaction with amine, hydrogen sulfide serving merely as inert solvent. In contrast, if thio anionic species were formed, exchange between solvent and original solute sulfurs could occur in either of the following two ways.

(1) In those experiments (*i.e.*, those with elemental sulfur and with group V sulfides, excluding preequilibrated phosphorus pentasulfide) where initial thio anion formation would involve interaction between solvent and solute, one being labeled (*cf.* eq 1), and where, further, the separation method was such as to involve decomposition of the thio anionic species to the initial solute, either partial or complete, a partial exchange would follow from any structural equivalence in the thio anion between solvent-derived and original solute sulfurs. For example, the formation of orthothiophosphate, $((C_2H_5)_3NH)_3PS_4$, followed by complete decomposition to P_4S_{10} (if no further exchange *via* (2) had occurred) would lead to a partial exchange observation of 37.5%

(2) Thio anion–solvent interactions in solution could provide one or more further exchange pathways. Such interactions might involve, for example, bimolecular processes, thio anion dissociation equilibria, or equilibria between alternative thio anionic species of different solvent sulfur content.

Wherever thio anion formation might be anticipated, the exchange has been found fast (though only moderately so with phosphorus pentasulfide) and essentially complete. In contrast, non-thio-anion-forming ethyl mercaptan showed no significant exchange rate. Such results, supplementing observations on solubilities, colors, and excess sulfur retention by recovered solutes, seem most readily understood in terms of, and so provide meaningful evidence for, the formation, in the basic solutions, of the anticipated thio anionic species, *viz.*, thioarsenate(III) and -(V), thioantimonate(III) and -(V), thiophosphate(V), thiocarbonate, and poly-

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sulfide. The completeness of the exchanges further suggests the occurrence of relatively rapid solute–solvent exchange interactions as suggested in (2) above.

Because of the high exchange rates, the data do not in general provide any indication of the specific chemical forms of the thio anionic species. Exceptions to this statement, however, are furnished by results with carbon disulfide at lower temperatures[16] and by the phosphorus pentasulfide data. The latter, where a measurably slow exchange was found, suggest, as already discussed, the occurrence of at least two thiophosphate forms, only slowly interconvertible and with quite different solute–solvent exchange rates, in the sense of (2) above. In analogy with the behavior of phosphates in water, one would suspect the initially formed, exchange-inert species to be of a condensed nature. The zero time exchange, presumably due to process 1 above, and apparently having a value between about 19 and 34%, would seem to support this hypothesis. Such a value appears more consistent with calculated figures for thio anions of lower sulfur–phosphorus ratio than orthothiophosphate (37.5%), such, for example, as pyrothiophosphate, $P_2S_7^{4-}$ (28.6%). The calculated zero exchange for a metathiophosphate, $(PS_3)_x^{x-}$ (17.7%), seems rather low, however, for this form to be, at least exclusively, the initial species. Whatever the first form, one would suppose the processes following the initial dissolving to tend toward a more fully solvolyzed species, presumably orthothiophosphate, this material then exchanging much more rapidly with the solvent than the initial substance. It is to be noted, however, that the equilibrated solution results suggest that solvolysis may possibly not be entirely complete, the equilibrium system still containing a certain concentration of a less solvolyzed (and more slowly exchanging) species.

The present experiments are of interest in both the contrasts and the parallels they present to analogous processes in aqueous systems. Thus, one may note the absence of rapid oxygen exchange with water of both phosphate[10a] and carbonate[24] ions and the contrasting fast exchange of arsenate ion.[10b] A further pertinent point is to be found in the slow interconversion of aqueous phosphate species and the observation of only slow radiophosphorus exchange rates between them.[25]

The elemental sulfur results seem generally consistent with those obtained with the other potential thio anion formers. The exchange rapidity, added to the solubility observations and contrasting with the nonexchange in neutral solution, appears to suggest polysulfide formation in the basic solutions. The results are of further interest in their parallel to the rapid and complete sulfur–sulfide exchange observed for aqueous polysulfide.[26] An additional interesting point is found in the rapidity of the exchange in the presence of only very minor concentrations of amine, a condition where almost all of the solute would be present as elemental sulfur, presumably S_8 rings, rather than polysulfide. This observation would appear to bear a distinct relationship to the observations of Bartlett and co-workers[27] relative to the cocatalytic effect of traces of hydrogen sulfide (or sulfur dioxide) on the catalysis by triethylamine of the reaction (in benzene) between elemental sulfur and triphenylphosphine. As postulated by Bartlett, *et al.*, we may suppose that, in the present system, reaction is brought about by very small concentrations of triethylammonium hydrosulfide functioning highly effectively in opening the S_8 rings.

These experiments have provided some interesting points of comparison between the solvent liquid hydrogen sulfide and its much more polar and associated analog water. While the differences between the two media are clearly marked, as, for example, in their relative solvent action toward ionic *vs.* covalent solutes, it appears to have been possible to establish a definite parallel in at least the particular case of the formation of thio anionic species in the present solvent, quite analogously to related processes in water.

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