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# Radiosulfur-Exchange Reactions in Liquid Hydrogen Sulfide. II. Kinetics of the Carbon Disulfide–Solvent Exchange in Triethylamine-Containing Solutions[1,2]

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The kinetics of radiosulfur exchange between carbon disulfide and the solvent liquid hydrogen sulfide in solutions containing triethylamine has been studied. Convenient half-times occur at −23°. The results are interpreted in terms of thiocarbonate formation in the solutions. Two alternative models fit the results about equally well. One postulates a relatively complete solute–solvent reaction yielding the substance $((C_2H_5)_3NH)(HC_2S_5)$, the exchange being first order in this species. The second model assumes formation at low triethylamine concentrations of an acid thiocarbonate, $((C_2H_5)_3NH)(HCS_3)$, this substance tending toward conversion to the normal form, $((C_2H_5)_3NH)_2CS_3$, at higher amine concentrations, and the exchange rate being first order in the acid form and independent (or nearly so) of the concentration of the normal form. In either case, thiocarbonate dissociation is taken to be the rate step. Equilibrium and rate constants have been obtained in terms of both models. The first, with negligible dissociation of $((C_2H_5)_3NH)(HC_2S_5)$ assumed, yields the activation parameters $\Delta H^* = 19.0$ kcal/mole and $\Delta S^* = 2.0$ eu.

In the preceding paper,[4] results have been reported of the study of radiosulfur-exchange reactions between various solutes and the solvent liquid hydrogen sulfide. Particularly interesting were a number of experiments in triethylamine-containing media suggestive of the formation of thio anions in solution. Since the exchange rates were in most cases too fast to follow, however, the results were generally only qualitative and, except to a degree with phosphorus pentasulfide, provided no evidence as to the specific chemical nature of the postulated thio anions. With the solute carbon disulfide, for example, thought to form thiocarbonate in solution, exchange at 25° was essentially complete within the time of the experiments. In this carbon disulfide system, however, it has been possible, by working at lower temperatures, to obtain measurable rates. The present paper constitutes a report of an investigation of the kinetics of this exchange.

## Experimental Section

Materials and methods were essentially the same as previously described.[4] Sulfur-35 was the tracer, and the solute carbon disulfide was labeled in all cases. The runs were made in sealed Pyrex ampoules, temperatures being maintained by use of appropriate slush baths (1,2-dichloroethane, carbon tetrachloride, or ice). The solutions showed a pale yellow to reddish orange color, depending on triethylamine or carbon disulfide concentration. The recorded molar concentrations were computed for the solution components as dosed out, any possible reaction (*e.g.*, thiocarbonate formation) being ignored and volume additivity for the mixed materials being assumed. Densities used were (g/ml, at −35.9, −23.0, 0.0, and 25°, respectively): (a) $(C_2H_5)_3N$,[5] 0.778, 0.766, 0.746, 0.723; (b) $CS_2$,[6] 1.346, 1.327, 1.293, 1.255; (c) $H_2S$,[7] 0.886, 0.866, 0.827, 0.771.

At the end of a run, exchange was assessed by distilling from the solution at −78° a small vapor sample, almost entirely hydrogen sulfide, other solution components being relatively less volatile. (Complete solvent evaporation left an easily decomposable solid, amber residue.) The solvent sample, precipitated as copper sulfide, was oxidized by sodium peroxide fusion to sulfur(VI) and precipitated as barium sulfate for counting. The fraction exchange was calculated as the ratio of the observed specific activity of this sample to that expected for complete exchange, the latter normally being computed, on the basis of relative reactant concentrations, from the initial carbon disulfide specific activity. The initial activity was obtained by conversion of a sample of the carbon disulfide to xanthate, oxidation with basic peroxide, and counting as barium sulfate. Occasional infinite time check experiments (>24 hr at room temperature) gave solvent sample activities which agreed satisfactorily with the calculated infinite time values.

Under each set of conditions a number of runs of various durations were made (usually about seven or more). The resulting fraction exchanges were plotted by least squares as log $(1 - F)$ *vs.* time. Although in certain cases some scatter occurred, the data appeared generally to conform reasonably well to the expected linear relationship; the occurrence of only a single exchange rate is thus implied, despite the presumed presence of carbon–sulfur species in more than one form. The recorded half-times were obtained from these plots, and exchange rates were calculated on the basis of the usual McKay relationship. The initial, "dosed" concentrations, computed as above described, of the two exchanging species, $CS_2$ and $H_2S$, were employed in the prelogarithmic term in the calculation (*i.e.*, any possible thiocarbonate formation again being ignored). Due account was taken of the presence of two exchange-equivalent sulfurs in carbon disulfide. In the interpretation of the results, any solution nonideality was ignored, all rate and equilibrium constant calculations being made in terms of solute concentrations.

## Results

**Rate Law I.**—The results of all the experiments are recorded in Table I. Convenient half-times were obtained at −23.0°, and a considerable number of experiments were run at this temperature, triethylamine and carbon disulfide concentrations being varied over significant ranges in an effort to obtain a rate law for the

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(3) Taken from the Ph.D. Thesis of J. R. Mickelsen, Oregon State University, June 1956.

(4) J. R. Mickelsen T. H. Norris, and R. C. Smith, *Inorg. Chem.*, **5**, 911 (1966).

(5) E. Swift, Jr., *J. Am. Chem. Soc.*, **64**, 115 (1942).

(6) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p 23.

(7) J. P. Baxter, L. J. Burrage, and C. C. Tanner, *J. Soc. Chem. Ind.* (London), **53**, 410 (1934).

Table I

Carbon Disulfide Exchange Rates in Triethylamine-Containing Hydrogen Sulfide

| Expt no. | $[(C_2H_5)_3N]$,[a] *M* | $[CS_2]$,[a,b] *M* | $[H_2S]$,[a] *M* | $10^{-3}t_{1/2}$, sec | $10^4$(rate), g-atoms $l.^{-1}$ $sec^{-1}$ | $10^4k$, g-atoms $mole^{-1}$ $sec^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | A[f] | B[g] | C[h] |
| Experiments at −23.0° | | | | | | | | |
| 1 | 0.042 | 0.39 | 25 | 34 | 0.153 | 3.6 | 3.9 | 6.7 |
| 2 | 0.042 | 0.76 | 24 | 50 | 0.197 | 4.7 | 4.8 | 6.8 |
| 3 | 0.037 | 2.5 | 22 | 230 | 0.125 | 3.4 | 3.4 | 3.8 |
| 4 | 0.034 | 3.9 | 19.6 | 240 | 0.160 | 4.8 | 4.8 | 5.2 |
| 5 | 0.33 | 0.37 | 24 | 9.5 | 0.53 | 2.8 | 3.6 | 4.3 |
| 6 | 0.32 | 0.73 | 23 | 8.9 | 1.06 | 3.3 | 4.0 | 5.9 |
| 7 | 0.32 | 1.02 | 23 | 13.3 | 0.98 | 3.1 | 3.2 | 4.7 |
| 8 | 0.29 | 2.4 | 21 | 23 | 1.21 | 4.2 | 4.2 | 5.0 |
| 9 | 0.26 | 3.8 | 19.0 | 30 | 1.25 | 4.7 | 4.7 | 5.3 |
| 10 | 0.75 | 0.35 | 22 | 5.4 | 0.88 | 5.0 | 5.8 | 5.5 |
| 11 | 0.72 | 0.97 | 22 | 8.7 | 1.41 | 2.9 | 3.3 | 3.9 |
| 12 | 0.66 | 2.3 | 19.8 | 9.1 | 2.8 | 4.3 | 4.3 | 5.8 |
| 13 | 0.60 | 3.6 | 18.1 | 16.5 | 2.2 | 3.6 | 3.6 | 4.4 |
| 14 | 1.10 | 0.33 | 21 | 7.1 | 0.63 | 3.8 | 4.2 | 4.2 |
| 15 | 1.07 | 0.65 | 21 | 5.0 | 1.70 | 5.2 | 5.7 | 5.6 |
| 16 | 1.83 | 0.29 | 18.8 | 6.2 | 0.64 | 4.3 | 4.8 | 6.0 |
| 17 | 1.80 | 0.58 | 18.5 | 7.0 | 1.09 | 3.8 | 4.0 | 4.6 |
| 18 | 1.78 | 0.82 | 18.3 | 6.4 | 1.63 | 4.0 | 4.2 | 4.5 |
| 19 | 1.65 | 1.98 | 17.0 | 5.2 | 4.3 | 4.3 | 4.6 | 5.1 |
| 20 | 1.53 | 3.1 | 15.7 | 5.5 | 5.7 | 3.7 | 4.0 | 5.6 |
| | | | | | Av | 4.0 | 4.3 | 5.1 |
| Experiments at Other Temperatures | | | | | | | | |
| 21[c] | 0.62 | 3.7 | 18.5 | 134 | 0.27 | 0.44 | | |
| 22[c] | 1.87 | 0.30 | 19.2 | 51 | 0.079 | 0.52 | | |
| 23[d] | 0.34 | 0.97 | 22 | ~0.43 | ~29 | ~85 | | |
| 24[d] | 0.66 | 0.93 | 21 | ~0.19 | ~62 | ~133 | | |
| 25[e] | 0.130 | 0.94 | 21 | <0.15 | >80 | >610 | | |
| 26[e] | 0.62 | 0.87 | 19.5 | <0.08 | >140 | >330 | | |

[a] Solution component concentrations as initially mixed, calculated without regard for postulated thiocarbonate equilibria. [b] Carbon disulfide initially labeled. [c] Temperature −35.9°. [d] Temperature 0.0°. Data have low reliability because of high rate. [e] Temperature 25°. Data from previous paper (ref 4). Data have low reliability because of high rate. [f] Based on eq 1 and 2; reaction 1 complete to the right. [g] Based on eq 1 and 2, the formation constant in reaction 1 taken as $K = 116$. [h] Based on eq 7–9, $K_1 = 3.4$ and $K_2 = 1.13$.

exchange. The calculated concentrations of the solvent hydrogen sulfide, varying only modestly, are also recorded in the table.

In preliminary analysis of the data, log–log plots were made of rate *vs.* first triethylamine and then carbon disulfide concentration for cases where each solute was present at low and varying concentration, the other being approximately constant and at relatively high concentration, *viz:* (1) $(C_2H_5)_3N$ varying, expt 4, 9, 13, 20 at $[CS_2] = 3.1\text{–}3.9$ *M;* (2) $CS_2$ varying, expt 16–20 at $[(C_2H_5)_3N] = 1.53\text{–}1.83$ *M*. The plots were linear with slopes of 0.88 and 1.02, indicating corresponding approximate apparent reaction orders relative to triethylamine and carbon disulfide, respectively. At first glance, these results might suggest a second-order reaction, first order with respect to each of the dosed solute concentrations. That such an inference is invalid, however, is immediately evident from further scrutiny of Table I, which shows that, while at low $(C_2H_3)_5N$ concentration and high $CS_2$ concentration, the rate is, in general, roughly proportional to the former, it is not, at the same time, proportional to the latter. Rather, it tends to be independent of the higher concentration component. The analogous situation likewise holds for low $CS_2$ and high $(C_2H_5)_3N$ concentrations. These points are illustrated, for low, approximately constant $(C_2H_5)_3N$ and excess, varying $CS_2$, by the three run sets: (1) 1–4; (2) 8, 9; and (3) 12, 13. In each set the rate is approximately independent of the varying $CS_2$ concentration; and for the three sets taken together it is essentially first order in the minor component, the average observed first-order constants for the sets being, respectively, $4.1 \times 10^{-4}$, $4.4 \times 10^{-4}$, and $4.0 \times 10^{-4}$ g-atom $mole^{-1}$ $sec^{-1}$. Similarly, for low, approximately constant $CS_2$ and excess, varying $(C_2H_5)_3N$, the stated relationship is illustrated by the run sets: (1) 10, 14, 16 and (2) 15, 17. Again, the rate varies little with the excess component but is essentially first-order in the minor one, the average first-order constants for the two sets being, respectively, $2.2 \times 10^{-4}$ and $2.2 \times 10^{-4}$ g-atom $mole^{-1}$ $sec^{-1}$.

The foregoing considerations show a rate dependent only on the concentration of the minor solution component. We interpret this observation as suggesting the exchange rate to be proportional to the concentration of a thiocarbonate solute species, formed by essentially complete reaction between the substances put into the solution. The concentration of this resulting thiocarbonate then would depend on the stoichiometrically limiting reactant. A possible clue as to the specific nature of the species is, further, provided by the first-order rate constants cited above. For limiting

$(C_2H_5)_3N$, the constant averages $4.2 \times 10^{-4}$, while, for limiting $CS_2$, it is $2.2 \times 10^{-4}$, only about half as great. If one assumes, however, the thiocarbonate species to be formed by reaction of two moles of $CS_2$ for each mole of $(C_2H_5)_3N$, a "corrected" limiting $CS_2$ constant, at $4.4 \times 10^{-4}$, would approximately equal the limiting $(C_2H_5)_3N$ value. Hence, we proposed, as a plausible interpretation of the data, the formation of a thiocarbonate by reaction (essentially complete) between one mole of $(C_2H_5)_3N$ and two of $CS_2$. The amount of $H_2S$ involved is not revealed by the data, but it seems reasonable to imagine a prior, essentially complete 1:1 reaction between amine and solvent to yield $((C_2H_5)_3NH)(HS)$. This would suggest the thiocarbonate species $((C_2H_5)_3NH)(HC_2S_5)$. The rate then would be first order in the concentration of this substance, possibly dependent on its dissociation rate; thus

$$((C_2H_5)_3NH)(HS) + 2CS_2 \rightleftharpoons ((C_2H_5)_3NH)(HC_2S_5) \qquad (1)$$

$$\text{rate} = k[((C_2H_5)_3NH)(HC_2S_5)] \qquad (2)$$

As a test of this postulated rate law, values of the first-order constant, $k$, have been calculated from all the observed $-23°$ rates. While the values (column 7A, Table I) show a certain amount of spread, it is plain that in general the constancy is satisfactory.

To see whether the spread among the column 7A rate constants could be reduced by introducing a limiting formation constant, $K$, for eq 1, we have subjected the data to a least-squares treatment. We define: (1) $a = [((C_2H_5)_3NH)(HC_2S_5)]_\infty$, the concentration, calculated from dosed quantities, for complete reaction according to eq 1; (2) $b = [((C_2H_5)_3NH)(HS)]_{xs}$, the concentration corresponding to excess amine, over that needed to give $[((C_2H_5)_3NH)(HC_2S_5)]_\infty$; (3) $c = [CS_2]_{xs}$, the corresponding excess $CS_2$ concentration. We further define: (4) $x$ = the concentration of $((C_2H_5)_3NH)(HC_2S_5)$ dissociated (reverse of eq 1); (5) $K$ = formation constant (eq 1); (6) $k$ = first-order rate constant (eq 2); (7) $R$ = exchange rate (eq 2). In terms of these quantities, one may readily derive, for excess $CS_2$

$$R/a = k - k/K\left[\frac{1 - x/a}{(c + 2x)^2}\right] \qquad (3)$$

and for excess $(C_2H_5)_3N$

$$R/a = k - k/K\left[\frac{K(1 - x/a)}{4a(b + x)}\right]^{1/2} \qquad (4)$$

To obtain values of the unknown constants, $k$ and $K$, the observed values of $R/a$ for all the $-23°$ experiments were plotted together against one or the other of the bracketed terms on the right in eq 3 or 4. The intercept and slope obtained from a linear least-squares fitting of the data yielded the two unknowns: $K = 116 \pm 67\ M^{-2}$ and $k = (4.3 \pm 0.2) \times 10^{-4}$ g-atom mole$^{-1}$ sec$^{-1}$. This calculation was carried out by successive approximations, starting with the substitution of trial $K$ and the associated (calculated) $x$ values in the bracketed terms. Clearly, the calculation supports the general postulate of a large formation constant. However, in view of the scatter of the data (*cf.* the large standard deviation of $K$), it is also clear that, quantitatively, the calculated $K$ value should probably be taken simply as a possible order of magnitude indication. To give a visual comparison of the possible merit of this limiting formation constant, the $a - x$ values calculated from it have been employed to compute apparent $k$ values on the basis of eq 2 (column 7B, Table I). The spread among the values shows no important decrease as compared to the column 7A figures, the experimental standard deviation amounting to 16.6% as compared to 17.4% for the latter.

**Rate Law II.**—Although the foregoing rate law fits the data reasonably well, an alternative model is also found to serve about equally well. For this alternative, one may assume the formation in the solution of the acid and normal thiocarbonates, $((C_2H_5)_3NH)(HCS_3)$ and $((C_2H_5)_3NH)_2CS_3$, with the exchange depending mainly (or entirely) on the dissociation rate of the former, the dominant species at low amine concentration. In addition, one assumes at higher amine concentrations a tendency toward conversion from the acid to the normal form, postulated to exchange more slowly (if at all). By appropriate choice of two equilibrium and two rate constants, one may obtain a satisfactory fit for the data.

The equations here involved, together with their associated equilibrium constants, are

$$((C_2H_5)_3NH)(HS) + CS_2 \overset{K_1}{\rightleftharpoons} ((C_2H_5)_3NH)(HCS_3) \qquad (5)$$

$$((C_2H_5)_3NH)(HS) + ((C_2H_5)_3NH)(HCS_3) \overset{K_2}{\rightleftharpoons} ((C_2H_5)_3NH)_2CS_3 + H_2S \qquad (6)$$

All "free" triethylamine has again been assumed combined (although this is not necessary) with solvent as the hydrosulfide. Solvent concentration and its variation (eq 6) have been ignored in the equilibrium. The data have been treated in terms of the exchange rate law ($R$ = rate)

$$R = k[((C_2H_5)_3NH)(HCS_3)] \qquad (7)$$

It has been assumed that any direct contribution of the normal thiocarbonate to the rate is negligible.

For treatment of the data according to this model we define: (1) equilibrium concentrations: $x = [((C_2H_5)_3NH)(HCS_3)]$ and $y = [((C_2H_5)_3NH)_2CS_3]$; (2) original dosed concentrations: $a = [(C_2H_5)_3N]$ and $c = [CS_2]$. In terms of these quantities one may readily derive

$$(a - 2y)/R = 1/k + (1/kK_1)[1/(c - x - y)] \qquad (8)$$

$$(a - x - 2y)[(kc/R) - 1] - 1/K_1 = K_2(a - x - 2y)^2 \qquad (9)$$

Values of the constants for the $-23°$ data were obtained from linear least-squares plots (by successive approximation) of these relationships. First, experiments at relatively high $x/y$ ratios (no. 1–9, 11–13, 19, 20) were plotted in terms of (8) to obtain $k$ and $K_1$ and then, using the values so found, $K_2$ was obtained by plotting experiments at lower $x/y$ ratios (no. 10, 14–18) in terms of (9). The values so obtained at $-23°$ are

$K_1 = 3.4 \pm 0.7\ M^{-1}$, $K_2 = 1.13 \pm 0.17\ M^{-1}$, and $10^4k = 5.3 \pm 0.5$ g-atoms mole$^{-1}$ sec$^{-1}$. On the basis of these equilibrium constants, values of the equilibrium quantities $x$ have been calculated for all 20 experiments, and from these values, together with the observed rates, individual apparent rate constants have been calculated for each experiment. The figures so obtained (column 7C, Table I) may be seen to show a spread roughly comparable to that of the previously presented rate constants (columns 7A and 7B), the experimental standard deviation here amounting to 16.4%.

The data have also been examined in terms of a model similar to that above, but with the rate expression further including a term first order in the normal thiocarbonate. The examination suggests that this procedure leads to no great improvement in the fit of the data and that, at most, the normal thiocarbonate rate constant would be but a fraction of that for the acid thiocarbonate.

**Temperature Dependence.**—In addition to the experiments at −23.0°, runs were made at −35.9 and 0.0°. The results, as well as those for 25° previously reported[4] (where the high rate prevented quantitative measurement), are recorded in Table I. To avoid equilibrium constant ambiguity, the temperature dependence of the rate has been examined in terms of the $((C_2H_5)_3NH)(HC_2S_5)$ rate law (eq 1, $K$ very large, column 7A data). Average values of $k$ for the three lowest temperatures give a good linear plot of log $k$ *vs.* $1/T$ (despite the limited reliability of the relatively high rate, 0° data). From this plot one obtains the activation parameters: $\Delta H^* = 19.0$ kcal/mole and $\Delta S^* = 2.0$ eu. One may also extrapolate the plot to calculate a probable approximate rate constant for 25°, $10^4k = 2200$ g-atoms mole$^{-1}$ sec$^{-1}$. This value is, as expected, somewhat greater than the experimentally estimated lower limits quoted in the table, but not excessively so.

## Discussion

The results, as presented, are consistent with the previous general conclusion[4] of thiocarbonate formation from carbon disulfide in amine-containing liquid hydrogen sulfide solutions. They are, further, consistent with either of two alternative reasonable models for the specific nature of the thiocarbonate or thiocarbonates formed.

Unfortunately, the data do not allow a choice between the two postulated thiocarbonate models. On the basis of the nature of aqueous carbonate species, one might be inclined to favor the second model. However, acceptance of this model would require that one also accept as coincidence the rather close 2:1 ratio of the apparent first-order rate constants observed with limiting amine as compared to limiting carbon disulfide concentration. Further studies designed to differentiate between the two models are desirable. A supplementary systematic spectrophotometric investigation of these colored solutions, for example, appears inviting. In addition further exchange experiments should be done both in liquid hydrogen sulfide solutions and also in another, exchange-inert solvent of low dielectric constant. The latter type of exchange study would be of value, first, to show whether comparable equilibria and exchange rates occur, and, second, if so, to make possible variation of the hydrogen sulfide along with the other concentrations. With the thiocarbonate-dissociation-controlled mechanism, the hydrogen sulfide concentration should be without effect in the rate step, influencing matters only *via* equilibria.

Actually, a preliminary exchange study of the second suggested type has already been made in this laboratory,[8] with the exchange participants here involved dissolved in the solvent benzene. The exchange does occur (in contrast to the lack of $H_2S$–$CS_2$ exchange in benzene in the absence of amine[9]) and with a rate not too different from that expected on the basis of the present research. An initial interpretation of the kinetics appears possibly to favor (at least for benzene solutions) the second over the first postulated exchange model, but definite conclusions must await further work.

It is of interest to compare the exchange results in the present system with those found by Mills and Urey[10] in the analogous system involving oxygen exchange between water and the collective species carbon dioxide, bicarbonate, and carbonate. In the latter system, oxygen exchange between water and carbon dioxide alone was found to be relatively rapid and to decrease in rate with increase in pH (and accompanying increase in $HCO_3^-/CO_2$ ratio). These results contrast sharply with those obtained in our work. Here exchange between carbon disulfide and solvent is unobservable in the pure solution (no base added) but, as base is added, occurs with increasing rate, to the point where the sulfur solution exchange rate exceeds that observed with an analogous aqueous solution containing primarily bicarbonate. For example, an experiment at 0°, involving 0.0265 $M$ $HCO_3^-$ and 0.00013 $M$ $CO_2$ (also 0.02676 $M$ NaCl—no effect on rate), showed an exchange half-time of 2300 min. An amine–carbon disulfide–hydrogen sulfide solution of analogous composition should show at 0° a half-time of about 4 min.

The reason for the difference in these two systems seems fairly clear. Mills and Urey showed that, in both $CO_2$-containing and bicarbonate-containing solutions, the exchange proceeded *via* hydration–dehydration of carbon dioxide, the exchange between hydrated carbonic acid and bicarbonate ion being fast. Only in quite basic, carbonate-containing solution did a pathway involving a direct carbon dioxide–hydroxide ion interaction to give bicarbonate become evident. In contrast, in the present system, the lack of exchange in the absence of amine is undoubtedly due to a negligible solvation rate for carbon disulfide. Relative to this feature, one would naturally infer that the equilibrium percentage solvation of $H_2CX_3$, already limited with carbon dioxide in water, is probably very slight indeed

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[8] T. M. Beasley, M.S. Thesis, Oregon State University, June 1961.

[9] D. L. Douglas, R. A. Cooley, and D. M. Yost, *J. Am. Chem. Soc.*, **71**, 3237 (1949).

[10] G. A. Mills and H. C. Urey, *ibid.*, **62**, 1019 (1940).

with carbon disulfide in liquid hydrogen sulfide. In amine-containing solutions, however, this relative instability of carbon–sulfur species works in favor of exchange for the present system, where the mechanism is thought to involve reversible thiocarbonate dissociation. The stability and low dissociation rate of bicarbonate would make for a much more limited exchange rate by this type of pathway.

With a view to making the foregoing picture more quantitative, we have tabulated in Table II some analogous rate and equilibrium constants for the carbon dioxide–water and carbon disulfide–hydrogen sulfide systems. The data for the first system are taken from the work by Faurholt,[11] the values being extrapolated either to 25 or −23° and the concentration of water being introduced. (Also the nonliquid nature of the system at −23° is ignored.) The $CS_2$–$H_2S$ data are derived from the present research and are tabulated in terms of an assumption of the validity of the second ($HCS_3^-$) exchange model. Any indicated ions in hydrogen sulfide solution would, naturally, occur almost entirely associated in ion pairs with triethylammonium ion. In this table, we see reflected both the lesser stability and the greater dissociation rate of thiocarbonate relative to carbonate, a situation consistent with the preceding qualitative discussion. We further see the thiocarbonate dissociation rate constant, even at −23°, to be comparable to the carbon dioxide hydration rate constant (at 25°). In the table we have also given a maximum solvation rate constant for carbon disulfide, calculated from the estimated minimum exchange half-time for nonamine solutions, given in the previous paper.[4] The value is, of course, quite small, much smaller than the carbon dioxide hydration rate constant. Worth noting, however, is the fact that the ratio of these two constants ($\sim 10^6$) is not greatly different from the ratio of the recorded rate constants for reaction of $OH^-$ with $CO_2$ as compared to $SH^-$ with $CS_2$ ($\sim 10^4$).

TABLE II

COMPARISON OF RATES AND EQUILIBRIA FOR OXYGEN[a] AND SULFUR COMPOUNDS

$$B + CX_2 \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} BCX_2$$

| B | $CX_2$ | $t$, °C | $k_2$, $M^{-1}$ sec$^{-1}$ | $k_{-1}$, sec$^{-1}$ | $K$, $M^{-1}$ |
|---|---|---|---|---|---|
| $H_2O$ | $CO_2$ | 25 | $1.0 \times 10^{-3}$ | $3 \times 10$ | $3 \times 10^{-5}$ |
| $H_2S$ | $CS_2$ | 25 | $<5 \times 10^{-10}$ [b] | | |
| $OH^-$ | $CO_2$ | −23 | $1.1 \times 10^{2}$ | $1.6 \times 10^{-7}$ | $7 \times 10^{8}$ |
| $SH^-$ | $CS_2$ | −23 | $3 \times 10^{-3}$ | $8 \times 10^{-4}$ [c] | 3 |

[a] Constants for oxygen compounds extrapolated from data in ref 11. Water concentration, included in rate and equilibrium expressions, taken as 55.5 $M$. [b] Calculated from data in ref 4. $H_2S$ concentration included in rate expression. [b] (Exchange rate constant) × 1.5.

The consistency between previous and present results, especially as reflected in the data tabulation in Table II, appears to support the general interpretation of the latter here presented. It is to be hoped that future work will help to resolve the ambiguity relative to the exact nature of the thiocarbonate species present.

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(11) C. Faurholt, *J. Chim. Phys.*, **21**, 400 (1924).

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# Methanol Exchange in Dilute Solutions of Neptunium(V) Ions by Nuclear Magnetic Resonance Spectroscopy

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The relaxation of the methyl and hydroxyl protons of methanol by neptunium(V) has been examined over the temperature range of −80 to +50°. The results indicate that the rate of methanol exchange between the coordination sphere of neptunium(V) and the bulk solvent is measurable and has a rate constant of $9.0 \times 10^4$ sec$^{-1}$ at 0°. $\Delta H^*$ and $\Delta S^*$ for this reaction are 7.5 kcal/mole and −8 eu, respectively.

## Introduction

For some time it has been known that paramagnetic ions reduce the transverse relaxation time, $T_2$. McConnell and Berger[1] and Swift and Connick[2] have derived relationships from modified Bloch equations for the determination of the rate of exchange of ligands between the paramagnetic metal ion and the bulk ligand. Representative reactions studied in this way are the exchange of water between the transition elements[2,3] and the exchange of ammonia[4] and thiocyanate[5] ion with nickel(II), as well as the exchange of methanol with the transition metal ions.[6,7]

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