The value obtained, $pK_0' = 9.8$, is in good agreement with the values found for the ionization of the ϵ-amino groups of polylysine ($pK_0' = 10.04$[25]) and of proteins.[24]

The spectrophotometric titration curve, at ionic strength 0.1, of the lysine–tyrosine copolymer IV resembles that of copolymer V. No measurements could be performed between pH 9.60 and pH 11.00, where the solutions became turbid. The maximum turbidity occurred at pH 10.20. Assuming that this pH corresponds to the isoelectric point, $\beta_{is} = 0.286$ is obtained from eq. 4b, introducing $pK_0' = 9.8$. Equation 3 gives 0.86 for α_{is}, from which 9.4 is calculated for pK_0 from eq. 4a.

The results described above clearly show that copolymers of α-amino acids with polar side groups may serve as suitable model compounds for the study of the influence of different factors such as over-all electric charge, size and shape of the relatively high molecular weight peptides on the dissociation of specific groups in the chain. Such studies may be of importance in the detailed analysis of the potentiometric titrations of natural peptides as well as of proteins. As the spectrophotometric titrations of the tyrosine residues in the copolymers investigated were found to be reversible, and no change in spectrum occurred on addition of urea, it is reasonable to assume that all the tyrosine hydroxyl groups of the copolymers synthesized are free to ionize. In the various tyrosine-containing copolymers investigated no hydrogen bonds involving tyrosine seem therefore to be present, at least in the pH range over which the phenolic hydroxyls ionize.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Exchange of Tritium between TCl and Toluene with and without Catalyst

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Mixtures of tritium-labeled HCl with toluene showed no isotopic exchange when heated at 140° for 40 hr. The addition of either NO_2 or $SnCl_4$ resulted in exchange even at room temperature. The rates at 25° appeared to be in agreement with the expression $d[TCl]/dt = -k[TCl][SnCl_4 \text{ or } NO_2]$ where $k = ca.\ 4 \times 10^{-4}$ l. moles^{-1} sec.$^{-1}$ for $SnCl_4$, and is somewhat higher for NO_2. The catalyzed exchange proceeded faster at 140°, with an apparent activation energy of 10 ± 4 kcal./mole in each case. Mixtures of tritium-labeled HCl with mesitylene at 140° gave erratic exchange, the rate in the absence of impurities always being less than 0.03% per sec. Solutions of $SnCl_4$ in toluene absorb ultraviolet light at higher wave lengths than either component alone and the spectrum is not altered by the addition of HCl.

Introduction

The isotopic exchange of hydrogen between deuterium chloride and benzene has been shown to occur in the presence of $AlCl_3$,[1-3] while fragmentary evidence on the reaction in the absence of catalysts[3,4] suggests that slow exchange may possibly occur at 50°. Brown and Brady[5] have investigated the interaction of HCl with aromatic hydrocarbons at −78°, interpreting their data in terms of weak π-complexes which would not lead to hydrogen exchange, in contrast to the σ-complexes proposed for the aromatic-HCl-$AlCl_3$[6] and aromatic–HF–BF_3[7] systems, in which the hydrogen atom of the hydrogen halide is bonded to a particular carbon atom. They also proposed that the formation of σ-complexes requires an appreciable activation energy. On the basis of studies of the exchange of hydrogen between deuterated aromatic compounds and aqueous acids Gold and Satchell[8-10] have postulated rapid formation of a conjugate acid, $(C_6H_5D)H^+$ ("outer complex," "π-complex") between the aromatic molecule and a proton, followed by a slow intramolecular rearrangement to $(C_6H_6)D^+$ with resultant exchange.

In the light of these hypotheses and the available data[3,4] it seemed possible that the hydrogen from HCl might be induced to form σ-complexes and give measurable rates of exchange with aromatic compounds even in the absence of a catalyst if sufficiently high temperatures and long times of reaction were used. If such exchange occurred the relative activation energies for reaction with hydrocarbons of different basicity (*e.g.*, benzene, toluene, xylene, mesitylene) would be useful in considering the relative nature of π and σ-complexes. The work reported here was initiated to test these speculations by studying the isotopic exchange of tritium between TCl and aromatic compounds. It was extended to obtain information on the exchange of tritium between TCl and toluene, with $SnCl_4$ present as a catalyst. Stannic chloride was chosen because it forms single phase systems with toluene and HCl. This property made it possible to determine whether exchange could occur in the absence of a separate, highly polar, catalyst phase, and to make experiments on the effect of catalyst concentration on the reaction rate.

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Experimental

Materials.—Tritium-labeled HCl was prepared by the exchange reaction between T_2 gas and dry HCl over a hot platinum wire at about 860°. Toluene (Eastman Kodak "white label," from sulfonic acid) was purified by fractional distillation in a Todd column, followed by distillation through P_2O_5 on glass wool in the vacuum system used for filling the reaction cells. Mesitylene (Eastman Kodak, "white label") was similarly distilled and dried. NO_2 from a gas cylinder was dried by passing through a P_2O_5–glass wool column. N_2O was prepared by heating NH_4NO_3, and was purified by successive exposures to ferrous ion, NaOH pellets, and P_2O_5. The $SnCl_4$ (J. T. Bakers Analyzed) was distilled through a P_2O_5–glass wool column and stored in the vacuum system.

Tritium Determinations.—The specific activity of TCl–HCl mixtures was measured with an ionization chamber, constructed from stainless steel according to a modification of the Borkowski design.[11,12] The insulators were constructed of Teflon and Lucite, and a Teflon ring was placed between the body of the chamber and the guard ring to prevent sparking at low pressures. The chamber was assembled with O-ring seals, and an O-ring connection to the glass tubing of the vacuum system was provided. A Beckman Instruments, Inc., vibrating reed electrometer was used to measure the ionization currents and to provide the 210 volts applied across the chamber. In typical experiments the amount of tritium used was 10 to 100 μc and the currents were 10^{-11} to 10^{-10} amp.

The first measurements in the ionization chamber were made on H_2 prepared by reduction of the HCl samples by hot zinc, using argon as the bulk counting gas. A method which avoided the necessity for a reduction of the HCl proved to be simpler and more reproducible, and was used in all of the work reported here.

When TCl is introduced into the counting chamber care must be taken to avoid errors due to its adsorption on the walls and connecting tubing and subsequent desorption into later samples of lower specific activity. For example, when argon containing 4×10^{-6} mole of tritiated HCl was introduced into a clean ionization chamber, the ion currents sometimes decreased with time to half their initial values, and significant currents were obtained on subsequently admitting inactive HCl to the chamber. The results could be explained by the presence of about 5×10^{-5} mole of readily exchangeable hydrogen in the walls of the chamber. Use of HCl at 15 cm. pressure in place of argon as the bulk counting gas solved the problem, since when this was done the amount of exchangeable hydrogen in the gas phase was much greater than that on the walls. The inactive HCl was admitted to the chamber following the active sample and was allowed to pass through all of the glass tubing to which the active sample had been exposed, in order to pick up tritium which had been held by the surfaces. Results reproducible within 10% were obtained by this technique. A plot of current *vs.* pressure of HCl reached a plateau at about 15 cm. pressure, in good agreement with the results of Dorfman[13] for oxygen.

Preparation of Reaction Mixtures.—The exchange reactions with TCl were carried out in Pyrex tubes of about 5-ml. capacity, equipped with break seals. These were flamed while evacuated to about 1 micron, and then "equilibrated" with a supply of tritiated HCl sufficient to fill all of the tubes on a manifold and to provide samples for specific activity determinations. When a sample of TCl just sufficient for one tube was introduced to a manifold of tubes which had not been equilibrated, its specific activity was reduced, by exchange with the walls, to a greater extent than was that of subsequent samples.

Following equilibration of the walls, toluene or mesitylene was distilled into one of the tubes on the manifold, the amount being measured by the decrease of the volume in the graduated reservoir where it was stored. An aliquot of the equilibrated tritiated HCl was then measured out, using a manometer and calibrated metering flask, and frozen down in the reaction tube with the aid of liquid air. Any other desired materials were then added and the cell was sealed off from the vacuum system.

Separation and Analysis of Reaction Mixtures.—After a reaction cell had been maintained at the desired temperature for the desired time it was attached through its break seal to the vacuum system at a point separated from the ionization chamber by two U-tube traps. The first of these traps was cooled to −80° to condense the toluene, and the second was surrounded with liquid air to condense the HCl. The amount of HCl recovered was measured by a manometer adjacent to the ionization chamber. There was good agreement between the amount metered out and that recovered except in the case of the tubes to which NO_2 had been added (Table I).

Samples of the tritiated HCl, which had been equilibrated with the manifold and used to fill the cells, were transferred through the vacuum system to the ionization chamber in order to obtain the initial specific activity, S_0, of the samples. Both in the case of these samples and of those which had undergone exchange the inactive HCl used as the bulk counting gas was added through the same tubing to recover any activity lost to the walls.

Correction for Exchange with the Pyrex Cell Walls at 140°.—A few reaction tubes were filled with tritium-labeled HCl alone, no hydrocarbon being added. After heating for various times at 140° the HCl from three of these gave specific activities of 0.88, 0.91 and 1.01 of that of the HCl used for the filling. The loss of activity shown in two of these cells was apparently due to loss of tritium by exchange into deeper layers of the glass walls where it was not recovered by "rinsing" with non-radioactive HCl in the analytical procedure. In the calculations for all the runs made at elevated temperatures, a correction of 10% was made to the observed value of S_0 to allow for this loss of activity to the walls. Most of the results on the exchange between TCl and toluene in the absence of a catalyst showed no decrease in specific activity of the HCl with successively longer times of standing, but the recovered HCl regularly had a specific activity of about 0.9 of its initial value, further indicating that this correction was justified.

Method of Calculation.—Because of the exceptionally large isotope effects which are possible, tritium exchange reactions cannot be treated by the usual exchange equations.[14–17] In order to avoid this difficulty the experiments reported here were all carried out with at least a 100 to 1 molar ratio of the initially inactive exchanging compound ($C_6H_5CH_3$) to the initially tritiated compound (HCl), so that the reaction $TCl + C_6H_5CH_3 \rightarrow C_6H_4TCH_3 + HCl$ would, if it occurred, go essentially to completion. Under these conditions the back reaction, which might have a different rate constant than the forward, would be negligible. Then, if the rate of transfer of T is proportional to the first power of the TCl concentration, the fraction of the residual TCl transferred per unit time is constant, *i.e.*, the absolute rate of transfer of T decreases exponentially with time, and one may write

$$\frac{-\mathrm{d}\ln S/S_0}{\mathrm{d}t} = k'$$

where S and S_0 are the specific activities of the HCl–TCl mixture at time t and zero time, respectively. For experiments of the type in question, where the sum (C) of the HCl + TCl in a reaction cell remains constant

$$\frac{\mathrm{d}\ln S/S_0}{\mathrm{d}t} = \frac{\mathrm{d}\ln S}{\mathrm{d}t} = \frac{\mathrm{d}\ln \mathrm{TCl}/C}{\mathrm{d}t} = \frac{\mathrm{dTCl}}{\mathrm{d}t}\,\frac{1}{\mathrm{TCl}} = -k'$$

so that k' is the fraction of the TCl which exchanges per unit time ("TCl" denotes total TCl in the cell). The value of k' is

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TABLE I

EXCHANGE OF TRITIUM FOR PROTIUM BETWEEN TCl AND TOLUENE IN THE PRESENCE OF CATALYSTS

All the runs were made in sealed Pyrex cells with 0.4 to 1.1 ml. of toluene present as the solvent.

	Concn., moles/l. HCl[b]			Time, min.				
v./l.[a]	Initial[c]	Final[d]	Catalyst NO_2[h]	at 25°	at 140°	S/S_0[e]	$k' \times 10^6$, sec.$^{-1}$[f]	$k \times 10^4$[g]
8.8	0.074	0.034	0.020	45	50	0.33	370	180
11.0	.074	.061	.0088	137	60	.48	208	240
9.4	.0244	.0178	.0046	82	120	.553	82	180
9.4	.076	.069	.0044	265	120	.61	68	150
8.8	.074	.072	.00024	278	220	.94	4.8	200
							Av.	1.9×10^{-2}
	.075	.068	.0030	2718	0	.668	2.5	8.3
9.4	.075	.072	.0012	4008	0	.806	0.77	6.5
							Av.	7×10^{-4}
			$SnCl_4$					
9.6	0.073	0.073	0.014	106	120	0.637	63	44
9.0	.074	.075	.55	376	0	.136	88	1.6
9.6	.073	.072	.090	1240	0	.205	21.5	2.4
9.8	.073	.072	.054[i]	1391	0	.311	14.0	2.6
8.6	.073	.073	.044	1088	0	.62	7.3	1.7
9.4	.141	.139	.040	2307	0	.264	9.6	2.4
5.0	.0384	.0385	.025	2836	0	.463	4.5	1.8
9.2	.069	.067	.014	8323	0	.194	3.28	2.3
5.5	.0268	.0268	.007	12686	0	.214	2.02	2.8
							Av.	2.2×10^{-4}

[a] v./l. is the ratio of vapor to liquid volume for each cell. [b] The values given are the moles of HCl divided by the liters of solution, neglecting the fact that some of the HCl is in the vapor phase. [c] The conc. of HCl listed in this column was calculated from the amount of HCl metered into the reaction cell. [d] Values in this column were calculated from the amount of HCl recovered in the separation. [e] S/S_0 is the specific activity of the HCl after the run (using the amount of HCl metered out) divided by the specific activity of samples from the same supply of tritiated HCl transferred directly to the ionization chamber. In all the runs at 140°, S_0 was corrected by a factor of 0.90 for exchange with the Pyrex walls of the cell. [f] k' is the rate of loss of tritium from the HCl divided by the amount of TCl present in the HCl. [g] k has units of l. moles^{-1} sec.$^{-1}$ and is calculated from the expression: $R = k'[\text{TCl}] = k[\text{TCl}][NO_2]$ or $R = k[\text{TCl}][SnCl_4]$. [h] Values in this column are the moles of NO_2 used divided by the liters of solution, neglecting any reactions of NO_2 which may have occurred. [i] This cell contained water. Enough H_2O was added to give a concentration of 0.023 M if it did not react with the $SnCl_4$.

a constant for a given cell filling at a given temperature,[18] but is smaller for a cell where the ratio of vapor to liquid volumes is larger, since the fraction of the TCl in the liquid phase at any moment during the run is smaller in the latter case.

Comparisons of different runs where reaction occurred were made on the basis of k' values obtained from the integral form of the above equation, $\ln S/S_0 = -k't$. Estimates of the absolute rates of exchange from such data give the rate of tritium exchange and not that of protium exchange, which may be different because of the isotope effect.

Results

Absence of Exchange between TCl and Toluene in the Absence of Catalyst.—Fourteen experiments using the techniques described above were made on the exchange of tritium between TCl and toluene in tubes to which no catalysts were intentionally added. These tubes were heated for various times at 140°. One of them gave a value of 1.12 for S/S_0 (after applying the 10% correction to S_0 for exchange with the glass walls) after 2220 min. at 140°, and seven others, after heating between 300 and 2430 min., gave values between 0.94 and 1.03, which are within experimental error of zero exchange. The other six cells showed some exchange, with values of k' ranging from 1.4×10^{-6} to 6×10^{-5} sec.$^{-1}$. It is much more likely that there was a trace of some catalyst in these cells than that there was enough of some inhibitor present in the other eight cells to stop completely the exchange. Therefore one can conclude that in the absence of catalytic impurities there is no appreciable exchange of tritium between TCl and liquid or gaseous toluene, at 140° or below, in times up to 2400 minutes.

There is not sufficient evidence available to identify the impurity responsible for the exchange observed in some of these tubes. Air and water were shown not to have sufficient catalytic effect to be responsible. However, the presence of 2×10^{-6} mole of NO_2 would be sufficient to give the largest rate found. This, or a similar material, might have come from the glass wool used in the P_2O_5 columns (this glass wool had been cleaned with hot nitric acid), or possibly from the action of a Tesla coil discharge on residual or adsorbed air in the vacuum system.

Toluene–TCl Exchange in the Presence of NO_2.—The results of a number of experiments on the exchange between TCl and toluene in reaction tubes to which NO_2 had been added are summarized in Table I. In all these runs the amounts of HCl

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(18) If the mechanism for exchange of H (or T) between HCl (or TCl) and $C_6H_5CH_3$ required more than one HCl and/or TCl molecule in the activated complex, and if there is an appreciable isotope effect in this reaction, then k' would change with changing specific activity at specific activities sufficiently high so that there was a significant probability of two TCl molecules entering the same activated complex. In the present work the ratio of TCl to HCl in the starting gas was sufficiently low to make this probability negligible. Hence if the rate of exchange was second order in the hydrogen chloride, the activated complexes containing tritium would always be of the form (HCl, TCl, $C_6H_5CH_3$) and k' would be independent of the specific activity. Presumably this point is of only incidental interest here, since the activated complex would be expected to involve only one HCl or TCl molecule.

recovered were less than the amounts originally metered out. The amounts of HCl lost were generally 1.5 to 2.3 times the amount of NO_2 added. The available thermodynamic data[19] indicate that the equilibrium $NO_2 + 2HCl \rightleftarrows NOCl + 1/2Cl_2 + H_2O$ lies far to the right at room temperature with the concentrations used in this work. If NOCl and Cl_2 were formed they may have reacted further with the toluene, but the possible amount of such reaction was too small to account for all the observed decreases in the specific activity of the HCl. Neglecting any isotope effect, about 7 moles of hydrogen was lost from the HCl, by exchange, for each mole of NO_2 added, in one of the reaction tubes. Thus NO_2 or some material produced when it is added apparently catalyzes the exchange between TCl and toluene. One run with H_2O added showed that it does not have enough catalytic activity to account for the observed rates. NOCl or Cl_2 or nitration products of the toluene may be responsible.

The rates of exchange were roughly proportional to the "concentration" of NO_2 added, so that the rate of loss of tritium from the HCl can be formally represented by $R = k\,[TCl][NO_2]$ with an average value for k of 0.019 ± 0.004 l. mole^{-1} sec.$^{-1}$ at 140°. A comparison with the value of k from the two runs at room temperature gives a value of 7 kcal. per mole for the activation energy of the "NO_2" catalyzed exchange of tritium between TCl and toluene. The interpretation of this value is quite uncertain because of the unknown change in the solubility of TCl and catalyst with temperature. The activation energy for the exchange with dissolved TCl will be greater than this observed value by some fraction of the heat of solution of TCl and catalyst and probably lies within the range represented by 10 ± 4 kcal. per mole.

In all the cells to which NO_2 had been added a red color was produced during the process of warming the cell from liquid air temperature. It disappeared before all the toluene had melted (m.p. $-95°$). The color was very intense, and it was clearly visible even in the cell with the lowest amount of NO_2, which did not give any visible yellow color at room temperature. When the HCl was separated from the toluene by distillation through a trap at $-80°$ into one cooled with liquid air, the ring of HCl formed in the second trap was red or pink from all these cells except the one with the least added NO_2. Similar color effects have been reported previously for mixtures of HCl and NO at liquid air temperatures,[20a,20b] for carefully purified HCl at liquid air temperatures[20c,20d] and for mixtures of NO or NO_2 with aromatic compounds in the presence of anhydrous acids.[20e] They have been attributed to the formation of unstable complexes,[20b,20e] and, in the case of purified HCl, to a metastable crystal structure[20c] or lattice imperfections.[20d] The present work indicates that the presence of NO_2 in HCl which is frozen down with liquid air induces a "red HCl" similar to that reported for purified samples.

N_2O does not produce any colors with HCl or catalyze the exchange of tritium between TCl and toluene.

Toluene–TCl Exchange in the Presence of $SnCl_4$.—The addition of $SnCl_4$ to solutions of TCl in toluene resulted in the exchange of tritium at an appreciable rate even at room temperature. These results are listed in Table I. Measured aliquots of $SnCl_4$ were obtained from a reservoir by thermostating it and allowing the vapor to fill a vessel of known volume at the known vapor pressure. The fact that the aliquoting method was not rigorously quantitative may account for some of the scatter shown by the data.

The rate of tritium transfer was, within experimental error, proportional to the concentration of $SnCl_4$. The addition of 0.023 mole/l. of H_2O to one of the cells which contained 0.054 mole/l. of $SnCl_4$ did not change the rate appreciably, so water is apparently not a co-catalyst for the exchange. It thus appears that the rate at 25° can be represented satisfactorily by the expression $R = k[TCl][SnCl_4]$, with a value of k of $2.2 \pm 0.6 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$, calculated as if all the HCl were in solution. Extrapolation from solubility values at $-78°$[5] and 0°[21] suggests that about half of the HCl was in the gas phase in these experiments at 25°. The value of the rate constant based on the dissolved HCl is, therefore, probably about 4×10^{-4} l. mole^{-1} sec.$^{-1}$. The one run at 140° suggests that the activation energy is about 6 kcal./mole. As with the runs catalyzed by "NO_2," discussed above, lack of information on the temperature coefficient of the solubility of TCl leads to some uncertainty in the interpretation of this activation energy. As before, the range 10 ± 4 kcal./mole probably includes the activation energy for the exchange with dissolved TCl. If the activated complex is considered to contain one molecule of toluene this leads to a value for the frequency factor of 10^{-1} to 10^{6} l.^{2} moles^{-2} sec.$^{-1}$.

The rates do not show any consistent trend with the value of the ratios of liquid to vapor volumes, v./l; however, this ratio was not varied sufficiently to give an adequate test of its influence.

The Spectrum of $SnCl_4$ in Toluene Solution.—A solution of HCl in toluene (about 0.02 M) showed the same spectrum as toluene alone; absorption began at about 3000 Å. and rapidly increased at shorter wave lengths. Cells containing $SnCl_4$ showed considerable absorption at longer wave lengths. This absorption was independent of time of standing and of the amount of HCl present. It started at about 3900 Å. and increased at shorter wave lengths with no evidence of a decrease before the toluene cut-off at 2800 Å. The extinction coefficients for $SnCl_4$ in toluene in units of l. mole^{-1} cm.$^{-1}$ were approximately: 1 at 3900 Å., 3 at 3800 Å., 30 at 3600 Å., 180 at 3400 Å., and 380 at 3300 Å.

Experiments on $SnCl_4$ in heptane solution in a quartz cell showed strong absorption below 2500 Å.

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[19] National Bureau of Standards circular 500, "Selected Values of Chemical Thermodynamic Properties," U. S. Govt. Printing Office, Washington, D. C., 1952.

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but no appreciable absorption above 2800 Å. Therefore the absorption observed in toluene is probably due to a complex between $SnCl_4$ and toluene and may be due to a charge transfer process of the type described by Mulliken.[22]

The Exchange of Tritium between TCl and Mesitylene.—Fifteen cells were filled with mesitylene and tritiated HCl. All the cells showed some decrease in the specific activity of the HCl even after the 10% correction for exchange with the walls at 140°. The rate of loss of the tritium was not reproducible. Values of k' ranged from 10^{-5} sec.$^{-1}$ to 3×10^{-4} sec.$^{-1}$ at 140°. The mesitylene exchange is apparently even more sensitive to traces of catalytic impurites than the toluene exchange.

Five of the cells, of which one was not heated above room temperature and four were heated at 140° for times up to 225 min., gave values of about 0.8 for S/S_0, and no higher values were obtained at 140°. This suggests that there is an impurity in the mesitylene which undergoes rapid exchange with TCl, while the mesitylene itself exchanges very slowly if at all in the absence of other impurities. One mole of an impurity with one exchangeable hydrogen atom per molecule, present in 300 moles of the mesitylene would be sufficient to reduce the value of S/S_0 to 0.8. This amount of impurity could easily have been present in the mesitylene used.

Discussion

The lack of exchange of tritium between TCl and toluene is in agreement with Brown's formulation of the interaction between HCl and aromatic hydrocarbons as involving weak π-complexes[5] and indicates that there is no accessible reaction path for formation of the σ-complex in the absence of a catalyst, even at 140°. The occurrence of exchange in the presence of $SnCl_4$ shows that there is some interaction between $SnCl_4$, TCl and toluene involving the formation of a carbon–tritium bond. This occurs in a homogeneous toluene solution, unlike the common Friedel–Crafts reactions which take place in the presence of a red oil phase which is presumed to favor reaction by an ionic mechanism because of its high dielectric constant. The exchange is not a high energy process since the activation energy is low. It has a very low steric factor or, equivalently, a large negative entropy of activation. This is probably what should be expected for an activated complex similar to the σ-complexes formulated by Brown[5,6] involving a considerable separation of charge, since such complexes may require a favorable orientation of the surrounding solvent molecules for their formation.

The spectrum of $SnCl_4$ in toluene indicates the formation of a complex between these two materials. Such a complex has been proposed by de Carli[23] on the basis of viscosity measurements, and solid complexes of $SnCl_4$ with some aromatic hydrocarbons have been observed.[24] The spectra of $SnCl_4$–HCl–$C_6H_5CH_3$ systems differ from those with $AlBr_3$–HBr–$C_6H_5CH_3$[25] in that no new peaks are observed on adding the hydrogen halide although rapid exchange of chlorine is known to occur between HCl and solid, liquid or gaseous $SnCl_4$.[26] There must be some interaction in the system $SnCl_4$–HCl–$C_6H_5CH_3$ to account for the tritium exchange, but any ternary complex either does not exist in appreciable concentration or does not give appreciable absorption above 3600 Å.

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The Crystal Structure of *n*-Dodecanoic Acid Hydrazide

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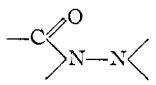
The crystal structure of *n*-dodecanoic acid hydrazide has been determined by two-dimensional projections. The structure consists of molecular ribbons held together by hydrogen bonds. These ribbons laid face-to-face make up the "molecular double layers" which are similar to those occurring in many long-chain compounds. Individual atom anisotropic temperature factor parameters have been determined for the projection on (010). They indicate electronic anisotropy of the chain atoms which corresponds to the direction of maximum thermal motion in projection essentially at right angles to the chain axis. Hydrogen atom positions have been determined and their precision indicated. Within the limit of experimental error, the chain is found to be planar and the C–C bonds, excepting those at the ends of the chain, of equal length.

A number of monoacyl derivatives of hydrazine are known to possess tuberculostatic activity. For these compounds it becomes a matter of some importance to know the exact stereochemistry of the molecule, in particular the precise configuration of



Kyame, Fisher and Bickford have shown that