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APPENDIX II

The normal coordinates and force constants calculated for the CH_3 group using the frequency assignments in Table I, the potential energy function given by Eq. (8), and assuming a value $f_{r\delta}=-0.212\times 10^5$ dynes/cm are:

Symmetric modes:

$$Q_1=0.717\times 10^{-12}(r_1+r_2+r_3)-0.107\times 10^{-12}R(\delta_{12}+\delta_{13}+\delta_{23})$$
$$Q_2=0.165\times 10^{-12}(r_1+r_2+r_3)+0.667\times 10^{-12}R(\delta_{12}+\delta_{13}+\delta_{23})$$
$$f_r=4.465\times 10^5 \text{ dynes/cm}$$
$$f_\delta=1.090\times 10^5 \text{ dynes/cm.}$$

Non-symmetric modes:

$$Q_3=0.848\times 10^{-12}(r_2-r_3)+0.069\times 10^{-12}R(\delta_{13}-\delta_{12})$$
$$Q_4=-0.185\times 10^{-12}(r_2-r_3)+0.550\times 10^{-12}R(\delta_{13}-\delta_{12})$$
$$Q_5=0.490\times 10^{-12}(2r_1-r_2-r_3)+0.040\times 10^{-12}R(2\delta_{23}-\delta_{12}-\delta_{13})$$
$$Q_6=-0.107\times 10^{-12}(2r_1-r_2-r_3)+0.318\times 10^{-12}R(2\delta_{23}-\delta_{12}-\delta_{13})$$
$$f_r=4.536\times 10^5 \text{ dynes/cm}$$
$$f_\delta=0.483\times 10^5 \text{ dynes/cm.}$$

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Chemical Reactions of Energetic Chlorine Atoms Produced by Neutron Capture in Liquid Systems*

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(Received January 13, 1950)

The fraction of the radioactive energetic chlorine atoms, formed by radiative neutron capture, that react with inactive carbon tetrachloride to give radioactive carbon tetrachloride, or with a solvent to give other radioactive organic halides, was studied as a function of composition in solutions of carbon tetrachloride in silicon tetrachloride, cyclohexane, and benzene. The reactions of similarly formed atoms were also studied for solutions of chlorine in cyclohexane and in benzene.

No significant effect of the temperature of the bombarded solution or of the energy of the neutrons was found.

The results are examined in terms of a theory which predicts the concentration dependence of some of the observed reactions, and alternative descriptions are suggested. It is concluded that the observed reactions occur before the recoil atoms are reduced to thermal equilibrium, and that particular reactions predominate in certain energy ranges.

INTRODUCTION

In 1934 Szilard and Chamers[1] found that about 60 percent[†] of the radioactive I^{128} formed in ethyl iodide by radiative neutron capture can be extracted from the organic liquid into a reducing aqueous solution. The similar treatment[2a, 2b] of several other organic halides showed that usually 40–60 percent of the halogen activity can be extracted from the irradiated organic liquid. Lu and Sugden[2c] determined the effectiveness of several different extractants for the bromine activity arising from the neutron bombardment of ethylene dibromide and bromobenzene. They found in both these cases that the most effective extracting solutions are those which will chemically remove elementary bromine from the organic liquid. By electrolyzing ethyl iodide after neutron bombardment, Fay and Paneth[2d] were able to collect about 60 percent of the activity on the anode when carrier iodide was present and the anode was of a material that reacts with halogens.

Libby[2b] has found that about 99.5 percent of the unextracted radioactivity formed in the (n,γ) reaction with bromine nuclei in bromobenzene exists as bromobenzene. However the chemical form in which the unextracted activity exists in some other organic halides has been shown by Gluckauf and Fay[2a] to include a considerable fraction of molecules in which the radioactive halogen has replaced a hydrogen. The replacement of a hydrogen atom by an active halogen was conclusively demonstrated by Reid[3] who found that the neutron irradiation of iodine dissolved in pentane resulted in the reaction of 30 percent of the radio iodine with the solvent to form active amyl iodide.

The results cited above evidently lead to the conclusion that a fraction of the molecules containing nuclei that have captured neutrons must break up as a consequence of the neutron capture and leave the active halogen in some form that can be extracted by an ap-

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[*] Research carried out, in part, under the auspices of the AEC.

[1] L. Szilard and T. A. Chalmers, Nature 134, 462 (1934).

[†] The fraction of the activity which is not extracted by the particular method employed has sometimes been termed the "retention." The word is occasionally used in this sense in the present paper. It is in general not synonomous with the more definite quantity, yield of a particular species containing radioactive material, with which we are principally concerned.

[2a] E. Gluckauf and J. W. Fay, J. Chem. Soc. 4, 390 (1936).

[2b] W. F. Libby, Science 93, 283 (1941).

[2c] Lu and S. Sugden, J. Chem. Soc. 7, 1273 (1939).

[2d] J. W. Fay and F. H. Paneth, J. Chem. Soc. 4, 384 (1936).

[3] A. F. Reid, Phys. Rev. 69, 530 (1946).

propriate aqueous solution. This fraction must at least equal the fraction of the activity that can be extracted, and may be greater.

The energy required for the molecular rupture is supplied by the recoil of the nucleus upon emission of a gamma-ray consequent to the capture of the neutron. If only a single gamma-ray is emitted, the energy of the recoil nucleus will be given by

$$E_R = (537E_\gamma^2)/m.$$

(E_γ is expressed in Mev, m is the mass number of the active nucleus, and the recoil energy is in ev.) Although this may be quite large compared to bond energies, (e.g., about 1.2×10^7 cal./mole for a 6-Mev gamma-ray from Cl^{38}), Suess[4] has pointed out that only a fraction of this energy will appear in the internal degrees of freedom of the molecule. This fraction is given by $M-m/M$, where M is the molecular weight of the compound. In all but the most extreme cases, however, bond rupture should occur. Various questions about energy partition in recoil processes have been discussed by Edwards and Davies.[5]

Since not all of the radioactive atoms can be extracted by an aqueous solution, it might be thought that molecular rupture does not occur in all the molecules that capture neutrons. This non-rupture could be due to a cancellation of gamma-ray momenta if the excited nucleus emits its excess energy in a cascade. However, it can be shown that unless a large number of gammas are emitted in the cascade sufficient cancellation is very improbable. Furthermore, the observation that the yield of extracted activity is altered either by adding[2c, 6] other compounds to the liquid being bombarded or by irradiating an organic halide[2a, 5, 6] vapor instead of a liquid shows that retention of activity, rather than being the result of a purely nuclear phenomenon, must have a basis in chemistry. Indeed, the evidence indicates that essentially all neutron captures will result in molecular rupture. The problem to be considered in this paper centers about the reactions by which the energetic radioactive fragment reenters a molecule.

The "liquid cage" model, suggested by Franck and Rabinowitch[7] to help explain low quantum yields in the photolysis of liquids, was used by Lu and Sugden[2c] for the interpretation of the reactions of the radioactive fragments. Their considerations involved the idea that the fragments of the ruptured molecule are trapped in a liquid cage and can either recombine or react with the solvent molecules in the wall of the cage. (The possible reaction of newly formed excited molecules with the solvent molecules was also suggested.) The recombination will leave the active halogen in the form of the parent compound, while a reaction with solvent molecules can give either new organic halides or halogen compounds that are extractable by an aqueous solution. These ideas were extended by W. F. Libby[8] who used the assumption that the collisions of the recoil atom are non-ionizing "billiard ball" impacts, and introduced as an energy parameter the minimum energy required for a radioactive atom to penetrate the walls of the "liquid cage." The predictions of this model, particularly in connection with the effect of varying the composition of the irradiated solutions, have subsequently been given by Miller, Gryder, and Dodson.[9]

The investigations to be described were directed toward an elucidation of the chemical reactions entered into by the radioactive Cl^{38} atoms formed through neutron capture by stable Cl^{37}, and in particular to furnish experimental results which can be compared with the existing theory[8, 9] of these reactions. It must be emphasized that in this research the only reactions examined were those involving the radioactive halogen. The reactions may have given rise to chains, but the products of the possible chain reactions were not found except insofar as they contained the active halogen. This was necessarily true as the sole evidence for the occurrence of a reaction was the presence of active nuclei in the appropriate products.

The nature of the phenomena studied makes it impossible to measure the rate of the reactions in the ordinary chemical kinetic sense. Instead one can only determine the relative yields of radioactive compounds formed in the various reactions of the recoil halogen atom. The yield of a given compound is defined as the fraction of the total radioactivity, of a specified isotope, that is found chemically indistinguishable from that given compound.

The variation of yield with the concentration of the reactants, temperature of the bombarded solution, and energy of the captured neutrons was investigated.

The yield of a given radioactive compound was determined experimentally by adding a carrier portion of the compound of interest to the irradiated solution, separating it, and comparing its chlorine activity with the total chlorine activity.

PROCEDURE

Counting Apparatus

To obviate the conversion of organic chlorides into precipitates such as AgCl, the activity of each sample was determined by counting a liquid solution of the active compound contained in a cylindrical jacket placed around, and coaxial with, an ordinary glass, thin-wall, argon-ethyl alcohol filled Geiger-Müller tube. Reproducible geometry was obtained by employing standard taper joints (male joint on the Geiger-Müller tube and female on the jacket) to support the jacket when in position around the counter. Inevitable differ-

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[4] H. Suess, Zeits f. physik. Chemie **B45**, 312 (1940).

[5] R. R. Edwards and T. H. Davies, Nucleonics **2**, 44–56 (1948).

[6] W. F. Libby, J. Am. Chem. Soc. **62**, 1930 (1940).

[7] J. Franck and E. Rabinowitch, Trans. Faraday Soc. **30**, 125 (1934).

[8] W. F. Libby, J. Am. Chem. Soc. **69**, 2523 (1942).

[9] Miller, Gryder, and Dodson, J. Chem. Phys. **18**, 865 (1950).

ences among the jackets were empirically corrected for with respect to the radiation detected. The maximum variation among the jackets was reflected in an effect of 6 percent on the counting rate.

The effect of the density of the liquid counted upon the self-absorbtion of the radiation was evaluated experimentally for the radiation from Cl^{38}. With the jackets and counter just described, a change in density from 1.0 to 1.6 decreased the counting rate by 19 percent.

Materials

The carbon tetrachloride, obtained from Eimer and Amend, was stated to be C. P. (passing A.C.S. specifications), sulfur-free, and had a boiling range of 76 to 76.5 degrees. The fraction retained after two distillations boiled over a range of 0.1 degrees.

The technical grade silicon tetrachloride obtained from Eimer and Amend was distilled twice in an open system and twice in vacuum. The fraction retained boiled over a range of 0.1 degree.

Cyclohexane from the Amend Drug and Chemical Company, Inc., which was stated to be C. P., was extracted three times with concentrated H_2SO_4, washed with distilled water, and dried first with Drierite and then with Na metal. The fraction retained, after a distillation from Na, boiled in a range of 0.2 degree.

The Eastman Kodak cyclohexylchloride used as a carrier was distilled once.

Baker and Adamson's thiophene-free, reagent grade benzene was dried for a week with Na and subsequently distilled over Na with the retained fraction boiling over a 0.2 degree range.

The carrier chlorobenzene, obtained from the Amend Drug and Chemical Company, Inc., was distilled once.

Methods

Carbon Tetrachloride-Silicon Tetrachloride Solutions.—Solutions of carbon tetrachloride in silicon tetrachloride were prepared in vacuum by distilling each component first into a bulb of calibrated volume and from there into a sample tube which was ultimately sealed. Thus the volume of the two components used in each sample was known. A few of the sealed tubes were kept for several weeks during which time there was no evidence of the formation of silicon dioxide.

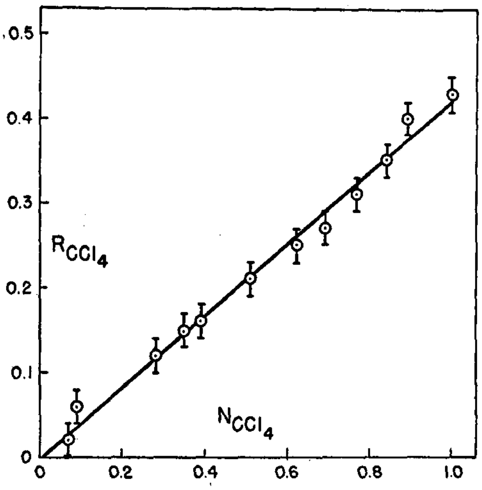

FIG. 1. The yield of radioactive carbon tetrachloride as a function of mole fraction carbon tetrachloride in carbon tetrachloride-silicon tetrachloride solutions.

TABLE I. The yield of radioactive carbon tetrachloride in solutions of carbon tetrachloride—silicon tetrachloride.

Mole fraction carbon tetrachloride	Active carbon tetrachloride
1.00	0.43
0.89	0.40
0.84	0.35
0.77	0.31
0.70	0.27
0.62	0.25
0.51	0.21
0.39	0.16
0.35	0.15
0.28	0.12
0.09	0.06
0.07	0.02

After the sample had been irradiated for about five minutes with neutrons (paraffin moderated) from the Columbia 37-in. cyclotron, the sample tube was broken open and the contents slowly dropped into an aqueous 6f sodium hydroxide solution. The solution was surrounded by an ice bath in order to minimize loss of carbon tetrachloride by evaporation. The sample tube was also washed with several portions of 6f sodium hydroxide, for it was found in preliminary experiments that up to 70 percent of the activity that can be extracted into the aqueous phase is adsorbed on the wall of the container used for the neutron irradiation. The washings were added to the aforementioned extracting solution, which contained at least 20 ml of base per ml of silicon tetrachloride in the original sample.

After the aqueous and organic phases were separated and made up to known volumes in volumetric flasks, a sample of each was drawn into a jacket and the counting rate determined at least five times during the course of two or three hours.

TABLE II. Yields in carbon tetrachloride-cyclohexane solutions.

Mole fraction carbon tetrachloride	Radioactive carbon tetrachloride	Radioactive chloro-cyclohexane	Summation organic yields	Total organic yield (experimental)
1.00	0.43	—	0.43	—
0.99	0.25	0.14	0.39	—
0.97	0.21	0.14	0.35	—
0.91	0.15	0.12	0.27	0.29
0.85	0.10	0.11	0.21	0.23
0.69	0.08	0.10	0.18	—
0.57	0.06	0.10	0.16	0.18
0.43	0.05	0.11	0.16	0.17
0.22	0.03	0.11	0.14	0.15
0.10	0.03	0.11	0.14	—
0.05	0.04	0.11	0.15	—

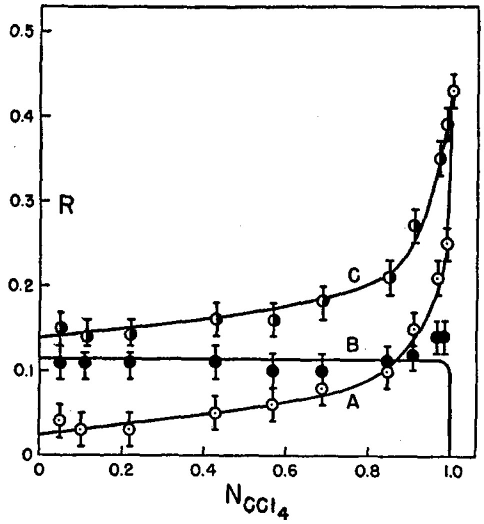

FIG. 2. The yields, R, of (A) radioactive carbon tetrachloride, (B) radioactive cyclohexylchloride, and (C) sum of (A) and (B) as functions of the mole fraction of carbon tetrachloride in carbon tetrachloride-cyclohexane solutions.

Carbon Tetrachloride-Cyclohexane Solutions.—The solutions to be bombarded were prepared by pipetting the desired volume of the components into 250-ml soft glass, glass stoppered bottles. Within five to fifteen minutes after removal from the neutron flux, 25 ml of 6f sodium hydroxide was added to the bottle in which the irradiation occurred and the mixture was vigorously agitated for several minutes. After the phases were separated, carrier chlorocyclohexane was added to the organic phase, which was subsequently fractionally distilled. The separated activities were then diluted and aliquots counted.

Carbon Tetrachloride-Benzene Solutions.—The procedure used with this system was similar to that outlined in the previous section, except chlorobenzene was used as a carrier instead of chlorocyclohexane.

Chlorine-Cyclohexane Solutions.—The solutions were prepared by bubbling dried chlorine gas through the hydrocarbon. The concentrations of solutions prepared in this manner were determined by thiosulfate titration of an aqueous iodide extract.

The solutions were bombarded in 100-ml volumetric flasks with stoppers waxed on so as to prevent appreciable loss of halogen by evaporation.

TABLE III. Counting rate of fractions taken during the distillation of carbon tetrachloride, cyclohexylchloride, and cyclohexane.*

Fraction	Counts per minute
1st 2 ml	403±15
2nd 2 ml	210±10
23rd 2 ml	240±14
28th 2 ml	248±15
2 ml out of last 10 ml left in pot.	238±13

* Starting solution contained 50 ml of carbon tetrachloride, 5 ml of cyclohexane, and 25 ml of carrier cyclohexylchloride.

Since in this case no attempt was made to distinguish between active cyclohexylchloride and any other activity that might be present in the form of a lower boiling organic chloride, the separation involved only extraction with 6f sodium hydroxide.

Chlorine-Benzene Solutions.—The procedure followed with this system was identical to that described in the preceding section.

RESULTS

Carbon Tetrachloride-Silicon Tetrachloride.—The yield of active carbon tetrachloride as a function of the mole fraction of carbon tetrachloride is given in Table I and in Fig. 1. An estimate of the counting and handling errors in this and all other experiments described, unless specifically stated otherwise, indicates a precision of 0.02 units in the measured values of the yields.

It is evident that the yield of radioactive carbon tetrachloride is very nearly proportional to the mole fraction of carbon tetrachloride in the irradiated solution. This is the result anticipated on the basis of the theory previously cited.[9] In sharp contrast is the behavior of systems containing hydrocarbons as diluents (see below).

The possibility of thermal exchange of chlorine between active carbon tetrachloride and inactive silicon tetrachloride was examined in order to ascertain if this process was affecting the results. Radioactive carbon tetrachloride was prepared by extracting an irradiated carbon tetrachloride sample with a sodium hydroxide solution. The remaining active carbon tetrachloride was washed with water, shaken for several minutes with Drierite, decanted, mixed with an equal number of moles of silicon tetrachloride, and allowed to stand for forty minutes. The separation was accomplished in the manner already described. The activity of the silicon tetrachloride fraction was found to be only one percent of what it would be if complete exchange had occurred; hence thermal exchange need not be taken into account in interpreting the results of these experiments.

Carbon Tetrachloride-Cyclohexane.—The yield of radioactive carbon tetrachloride and cyclohexylchloride as a function of N (mole fraction of carbon tetrachloride) is given in Table II and plotted in Fig. 2. The first column of Table II gives N, the second column gives the yield of radioactive carbon tetrachloride, the third gives the yield of radioactive cyclohexylchloride, the fourth gives the total organic yield as calculated by summing columns two and three, and the fifth gives the total organic yield

TABLE IV. Yields at different temperatures in carbon tetrachloride-cyclohexane.*

Temperature	Active carbon tetrachloride	Active chlorocyclohexane
25°C	0.06	0.10
0°C	0.07	0.12

* Mole fraction carbon tetrachloride 0.57.

TABLE V. Yields in carbon tetrachloride-benzene solutions.

Mole fraction carbon tetrachloride	Active carbon tetrachloride	Active chlorobenzene	Organic yield
1.00	0.43	—	0.43
0.99	0.30	0.12	0.42
0.97	0.27	0.16	0.43
0.92	0.23	0.22	0.45
0.90	0.22	0.24	0.46
0.82	0.17	0.21	0.38
0.65	0.12	0.22	0.34
0.53	0.12	0.22	0.34
0.38	0.10	0.20	0.30
0.29	0.08	0.18	0.25
0.23	0.06	0.20	0.26
0.15	0.07	0.20	0.27
0.08	0.06	0.18	0.24

as determined experimentally (fraction of activity retained in organic phase after aqueous extraction). Comparison of columns four and five indicates a satisfactory conservation of activity during the distillation process and lends support to the precision claimed above.

The apparent yield of active carbon tetrachloride does not seem to go to zero as the mole fraction of carbon tetrachloride approaches zero. This probably indicates the formation of some lower boiling organic chloride. Further evidence on this point is found in Table III, which gives the results of an experiment in which a fractionation of the higher and lower boiling products was performed. The data indicate that 97 percent of the active lower boiling component exists as carbon tetrachloride and essentially all of the higher boiling activity is cyclohexylchloride. It is possible, therefore, that about 3 percent of the activity in the carbon tetrachloride fraction was actually in the form of a lower boiling substance.

Since one of the important questions in the interpretation of "hot-atom" reactions is the assignment of the energy interval in which the reactions occur, it seemed desirable to make measurements at different temperatures. The results of such an experiment are given in Table IV. It is seen that a temperature change of 25°C has no effect within experimental error.

Carbon Tetrachloride-Benzene.—The very rapid drop in yield of active carbon tetrachloride caused by the addition of cyclohexane, in contrast to the effect observed upon the addition of silicon tetrachloride, was entirely unexpected in terms of the physical impact theory.[9] In order to find out more about this effect, it seemed desirable to vary the hydrogen-carbon ratio of the diluent, and for this purpose experiments were performed with benzene as a diluent. The results are presented in Table V and Fig. 3, which give the active carbon tetrachloride and chlorobenzene yields as functions of the mole fraction of carbon tetrachloride. The first column of Table V gives the mole fraction of carbon tetrachloride, the second and third columns give the yields of active carbon tetrachloride and chlorobenzene respectively, and the last column gives the total organic yield as determined by summing columns two and three. In spite of the physical and chemical differences of this diluent, the yield curves are seen to be qualitatively similar to those observed with cyclohexane.

The results of a fractionation of the higher and lower boiling fractions of one of the solutions indicate that 90 percent of the active lower boiling fraction is carbon tetrachloride and 88 percent of the active higher boiling fraction is chlorobenzene. These data are presented in Table VI. As in the carbon tetrachloride-cyclohexane system, the apparent yield of active carbon tetrachloride does not go to zero with the mole fraction of carbon tetrachloride. Taken in conjunction with the data in Table VI, this is again evidence for the formation of a small amount of a lower boiling organic chloride.

The effect of temperature upon the yields in carbon tetrachloride-benzene solutions was examined with the results given in Table VII. Again no significant difference is found between the results at room temperature and those at ice temperature.

Chlorine-Hydrocarbon Solutions.—Free chlorine was substituted for carbon tetrachloride in a series of experiments in order to check the assumption that the initial state of combination of the atom capturing a neutron has no effect on its subsequent fate except insofar as the free atom reacts with molecules of the parent type.

The total organic retention (fraction of activity not extractable) after neutron bombardment of chlorine dissolved in cyclohexane is given in Table VIII. Analyses of the chlorine solutions before and after bombardment showed that no significant loss of chlorine occurred during the irradiation.

The retentions are slightly higher than expected from the results with carbon tetrachloride, but it is believed that the differences are not significant.

In contrast to the behavior of chlorine-cyclohexane

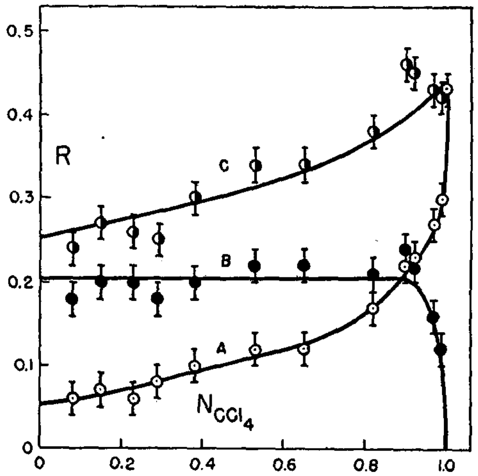

FIG. 3. The yields, R, of (A) radioactive carbon tetrachloride, (B) radioactive chlorobenzene, and (C) sum of (A) and (B) as functions of the mole fraction of carbon tetrachloride in carbon tetrachloride-benzene solutions.

TABLE VI. The counting rate of fractions taken during the distillation of carbon tetrachloride, chlorobenzene, and benzene.*

Fraction	Counts per minute
1st 15 ml	23,866±240
2nd 15 ml	18,146±200
3rd 15 ml	17,000±180
7th 10 ml	8,966±100
9th 10 ml	7,500± 95
last 10 ml	13,066±140

* Starting solution contained 50 ml of carbon tetrachloride, 5 ml of benzene, and 50 ml of carrier chlorobenzene.

TABLE VII. Yields at different temperatures in carbon tetrachloride-benzene.*

Temperature	Active carbon tetrachloride	Active chlorobenzene
25°C	0.12	0.23
0°C	0.13	0.26

* Mole fraction carbon tetrachloride 0.53.

TABLE VIII. Total organic retention in chlorine-cyclohexane solutions.

Mole fraction chlorine	Total organic retention
0.003	0.20±0.06
0.022	0.17±0.02

solutions, the total organic retention with chlorine-benzene solutions is markedly dependent on the concentration of chlorine, even in dilute solutions, as indicated by the data in Table IX. At mole fraction 0.001 the retention is not significantly different from that found with carbon tetrachloride-benzene at infinite dilution.

Further Examination of the Higher Boiling Radioactive Compounds Formed in Benzene.—The marked concentration dependence of the total retention in dilute chlorine-benzene solutions suggested the formation of active species other than chlorobenzene. Indeed this might be expected from what is known about the photochemical behavior of chlorine-benzene solutions. Noyes *et al.*[10] have found that the main product of the photolysis, at moderate chlorine concentrations, is a solid material that ranges in composition from $C_6H_6Cl_6$ to C_6Cl_{12}. Chlorobenzene is also found with a relative yield that increases with decreasing chlorine concentration. Hence, these materials were added as carriers after neutron irradiation in an examination of the higher boiling fraction in the chlorine-benzene system and a reexamination of this fraction in the carbon tetrachloride-benzene system.

The mixture of chlorinated benzenes was prepared by illuminating a solution of chlorine in benzene with radiation from a mercury discharge lamp.

Thus, in neutron irradiated solutions of chlorine in benzene and carbon tetrachloride in benzene the activity, after base extraction, was examined in three fractions; a fraction containing carbon tetrachloride and benzene, a fraction containing chlorobenzene, and the fraction remaining with the solid product of the photolysis.

The yields of chlorine activity in the three fractions are given in the first row of Table X.

A comparison of the first and second rows of Table X indicates a significant difference in the nature of the reactions giving higher boiling activities in these two systems.

In agreement with the data of Table VI, it is found that about 90 percent of the higher boiling active compound in the carbon tetrachloride-benzene system is chlorobenzene.

The Effect of Neutron Energy Upon the Retention to CCl_4.—The examination of the effect of the energy of the captured neutron upon the reactions of the recoil atom is made difficult by the decrease in the radiative capture cross section with increase in neutron energy which magnifies the effect of stray slow neutrons. An attempt to circumvent this difficulty was made by removing all paraffin moderator and surrounding the bombarded sample with Cd sheets and B_2O_3. Four determinations of the total retention to CCl_4 under these conditions showed no significant deviation from the retention found with moderated neutrons. Thus no evidence of an energy effect is found in this experiment.

DISCUSSION

As stated previously, the recoil from gamma-emission very probably results in the rupture of every carbon tetrachloride molecule in which neutron capture by chlorine occurs. The nature of the primary fragments from carbon tetrachloride has never been directly studied; however, Wechsler and Davies[11] have tenta-

TABLE IX. Total organic retention in chlorine-benzene solutions.

Mole fraction chlorine	Total organic retention
0.00095	0.16±0.08
0.0010	0.20±0.02
0.0090	0.39±0.02
0.015	0.43±0.02
0.040	0.54±0.02

TABLE X. Yields in chlorine-benzene and carbon tetrachloride-benzene solutions.

Solution	Relative activity in lower boiling fraction	Relative activity in chlorobenzene	Relative activity in solid carrier
Chlorine* in benzene	0.01	0.08	0.35
Carbon tetrachloride** in benzene	0.12	0.22	0.02

* Mole fraction chlorine 0.015.
** Mole fraction carbon tetrachloride 0.65.

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[10] Smith, Noyes, and Hart, J. Am. Chem. Soc. 55, 4444 (1931).

[11] S. Wechsler and T. H. Davies, Brookhaven Conference on the Chemical Effects of Nuclear Transformations, BNL-C-7, Appendix.

tively reported a positive charge on about 20 percent of the active fragments resulting from neutron bombardment of ethyl bromide in the vapor phase. The fraction of the active fragments with charge was different for the two active isotopes of bromine; and these investigators suggest that the charge is due to internal conversion of soft gamma-rays from the excited bromine nuclei. It is not known whether the gamma-rays from the excited Cl^{38} nuclei are internally converted. If internal conversion does not occur it is reasonable to assume that the active fragment is a chlorine atom rather than a positive or negative ion. This assumption is plausible since the motion of a 400-ev chlorine nucleus is quite slow compared to orbital electron motions. Thus the perturbation due to the nuclear recoil will be adiabatic and the probability of electronic transitions will be small. However, even if internal conversion does occur, the fact that the first ionization potential of atomic chlorine is thirteen volts[12] whereas the appearance potential of unipositive carbon tetrachloride is eleven volts[13] would insure the rapid neutralization of positive chlorine ions. We will therefore assume that in the systems studied, active chlorine atoms are formed at a high energy (*ca.* 400 ev) and in the process of cooling, or after having cooled, these atoms enter into chemical reactions which lead to their incorporation into the various molecular species observed.

If it is accepted that every neutron capture results in molecular rupture, the point of departure for any considerations on the reactions which form stable molecules must depend upon whether these reactions occur with active species in thermal equilibrium with their surroundings, or whether the energy distribution of the reacting active atoms is governed by the cooling process. If the latter case is correct, it is of further interest to know the energy range in which the reactions occur. The lack of temperature dependence exhibited in Tables IV and VII, and also found by Lu and Sugden[2c] in other systems, can be taken as support for the latter case.[‡, 14] It is of course possible, in the case of several competing reactions, that the lack of temperature dependence arises from an essential equality of the activation energy for these competing reactions, but this is not very probable. It is further worthy of mention that reactions occur with these hot atoms which do not occur thermally or photochemically. An example of this is an experiment of Rollefson and Libby,[15] who illuminated active chlorine dissolved in inactive carbon tetrachloride. It was found that after enough light had been absorbed to dissociate every chlorine molecule four times, there was no activity found as carbon tetrachloride. This is in contrast to the experiments just described in which 43 percent of the active chlorine atoms exchange with the carbon tetrachloride in the absence of other molecular species. Evidently, therefore, the exchange reaction between atomic chlorine and carbon tetrachloride occurs with chlorine atoms having an energy spectrum governed by the slowing down process, and in an energy range substantially above thermal.

With these assumptions the yield of radioactive carbon tetrachloride can be formally expressed as follows:

$$R=\int_0^\infty pN(E)W(E)dE, \qquad (1)$$

where p is the probability that a collision of an active chlorine atom is a collision with a carbon tetrachloride molecule, $N(E)dE$ is the number of active chlorine atoms making collisions per unit time in an energy interval dE at E (this is taken as a steady state quantity normalized to one hot atom formed per unit time), and $W(E)$ is the probability that the exchange reaction occurs in a collision with a carbon tetrachloride molecule at energy E. We may assume that below some critical energy, $W(E)$ will vanish. This critical energy can be considered as the activation energy for the reaction, although it is not necessarily identical with the activation energy determined in the conventional manner. It seems unlikely that collisions at very high energy will lead to stable chemical binding, in other words, we expect $W(E)$ to become small in the upper part of the energy interval.

The only existing theory that enables one to express $N(E)$ and $W(E)$ as explicit functions of the energy is one based on proposals by W. F. Libby.[8] The model employed in this approach (which will hereinafter be designated as the "physical impact theory") for reactions in the high energy range, involves non-ionizing billiard-ball collisions as the mechanism for energy loss of the "hot atoms" and introduces a second critical energy parameter, the minimum energy required for an atom to escape a liquid cage. This model was employed by Miller, Gryder, and Dodson[9] to evaluate $N(E)$ and $W(E)$ in Eq. (1) and thereby calculate R. The calculation was mainly concerned with the influence of other molecular species on the yields of given compounds into which the recoil atom may be incorporated. This influence manifests itself in the terms $N(E)$ and p. Some results immediately derivable from this treatment are given in Fig. 4. The curves show the yield of active carbon tetrachloride calculated for different assumed conditions, plotted against the probability that the impact partner in a collision is a chlorine atom in a carbon tetrachloride molecule. Curve A refers to the system carbon tetrachloride-silicon tetrachloride. In the calculation of curve A it is assumed that the carbon and

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[12] W. Latimer, *Oxidation Potentials* (Prentice-Hall, Inc., New York, 1948), p. 14.

[13] R. F. Baker and J. T. Tate, Phys. Rev. **53**, 683 (1938).

[‡] It should be noted that a pronounced difference in the yields of dibromipropanes formed in the neutron irradiation of isopropyl bromide at 25°C and at −196°C has been reported (see reference 15). Whether this is principally a temperature effect or a phase effect has not yet been established.

[14] L. Friedman and W. F. Libby, Conference on the Chemical Effects of Nuclear Transformations, BNL-C-7, and J. Chem. Phys. **17**, 647 (1949).

[15] G. K. Rollefson and W. F. Libby, J. Chem. Phys. **5**, 569 (1937).

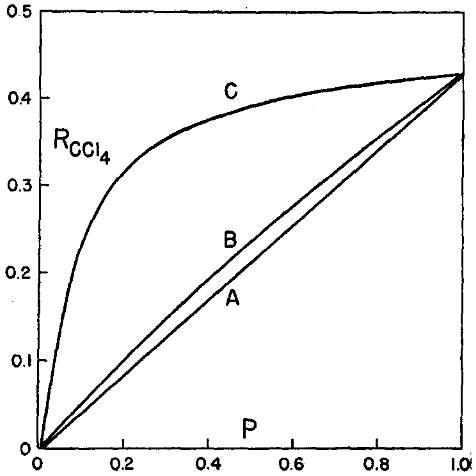

FIG. 4. The yield, R_{CCl_4}, of radioactive carbon tetrachloride predicted by the physical impact theory as a function of the probability that collision of a radioactive chlorine atom is a collision with a carbon tetrachloride chlorine atom in solutions of (A) carbon tetrachloride-silicon tetrachloride (ignoring collisions with carbon or silicon atoms), (B) carbon tetrachloride-hydrocarbon (ignoring collisions with hydrogen atoms and carbon-tetrachloride carbon atoms), (C) carbon tetrachloride-hydrocarbon (ignoring collisions with the carbon atoms).

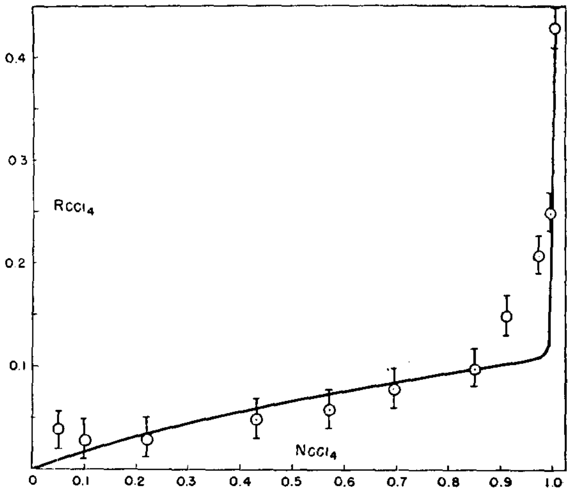

FIG. 5. A comparison of the yield of radioactive carbon tetrachloride as predicted by the physical impact theory (after allowing for the reactions with cyclohexane) with the experimentally determined yield (after correcting for the lower boiling activity that is not carbon tetrachloride) in the carbon tetrachloride-cyclohexane system.

silicon atoms are completely shielded and do not participate significantly in collisions, and thus that every impact partner is a bound chlorine atom. Curves *B* and *C* refer to the carbon tetrachloride-hydrocarbon systems with different assumptions as to the effective impact partners. Curve *B* takes into account only collisions with bound chlorine atoms and with carbon atoms. (A quite similar curve is obtained if hydrogen atoms are also included.) Curve *C* takes into account only collisions with bound chlorine and with hydrogen atoms, i.e., it is assumed that carbon atoms in the hydrocarbon are completely shielded by hydrogen.

The curves in Fig. 5 are not immediately comparable with the experimental curves in Figs. 1–3, since in the latter the abscissas are the mole fraction of carbon tetrachloride instead of the probability that a collision partner is of a specified type. The appropriate transformation from mole fraction to probability is

$$P_i = \frac{N_i\sigma_i}{\sum_j N_j\sigma_j},$$

where the subscript i designates a given atomic species present in a given molecular species, and j runs over all atomic species present in each type of molecule. N represents mole fraction and σ the collision cross section for a given atomic species (distinguished by subscript) in the given molecule. The cross sections introduced here refer to impacts which occur at high energy so that it is not proper to equate them to the cross sections calculated from interatomic distances or from van der Waals radii. However, since p is determined by the ratios of cross sections it is probably a fair approximation to employ bond radii in this calculation. The physical impact theory does not provide a means of estimating the absolute value of the yield since the parameters which enter (essentially given by the yield found when pure parent compound is irradiated) can at present be determined only by experiments of the type reported here. The significant comparison is that of the form of the yield curves.

If the impact cross section of chlorine is assumed to be the same in silicon tetrachloride and in carbon tetrachloride, the experimental curve in Fig. 1 is directly comparable to curve *A* in Fig. 4 (since their abscissas become identical); and there is seen to be good agreement between experiment and theory.

Unfortunately, however, no plausible combination of cross-section magnitudes has been found which will bring the carbon tetrachloride yield curves for cyclohexane or benzene solutions (Figs. 2 and 3) into agreement with either curve *B* or curve *C* of Fig. 4. It is evident that curve *C* (the case of hydrogen atoms shielding the carbon atoms) is made untenable. That this is so is not surprising since the maximum angular deviation in the path of a chlorine atom elastically scattered by a hydrogen atom is only 1/38 radian; hence the shielding of the carbon atoms by hydrogen atoms must be quite small.¶ But it is also apparent that the theoretical curve *B* lacks an important feature of the two experimental curves, *viz.* the very rapid decrease in yield of active carbon tetrachloride upon the addition of small amounts of hydrocarbon.‖

¶ This was kindly pointed out to us by Professor W. F. Libby.

‖ Lu and Sugden (reference 2c) observed a similar effect when aniline is added to organic halides and ascribed it to a Menschutkin type reaction between a newly formed radioactive molecule of the parent species and an aniline molecule in the cage wall. However, the very similar result observed in the present work with hydrocarbon diluents indicates that the effect may not be correlated with any familiar reaction which occurs at thermal energies.

Since the addition of small amounts of hydrocarbon should not produce a drastic decrease in p (Eq. (1)), nor should it have a large effect upon $W(E)$ (this point will be amplified below), it is indicated that the addition of small quantities of hydrocarbon causes a rapid decrease of $N(E)$ in the energy region where $W(E)$ makes an important contribution. The physical impact theory[9] predicts just the contrary effect upon $N(E)$, and furthermore does not account for the replacement of a hydrogen atom by an active halogen in any appreciable yield; hence it is appropriate to inquire whether there is any connection between these two discrepancies. A clue to the rapid drop in yield of active carbon tetrachloride may well lie in the equally rapid rise of the yield of active hydrocarbon chloride taken in conjunction with the essential lack of dependence of the hydrocarbon chloride yield on the composition of the solution below $N \fallingdotseq 0.90$. The constancy of the hydrocarbon chloride yield suggests that the chlorine atoms which react with the hydrocarbon diluent to give hydrocarbon chloride are atoms that are not capable of reacting efficiently with carbon tetrachloride to give stable compounds; otherwise competition should result in composition dependence. Further, at no time in their immediately previous history has reaction with carbon tetrachloride been very probable. This leads to the hypothesis that the fomation of radioactive hydrocarbon chloride is the first reaction that the active chlorine atom can participate in with appreciable probability while in the process of losing energy by collision. On this picture one is led to assume that every active chlorine atom reacts with hydrocarbon to give an excited intermediate complex which then decomposes to yield either active hydrocarbon chloride (or possibly active hydrogen chloride), or the original active chlorine atom which can then participate in other reactions. For if this were not true, the fraction of these atoms that so react with the hydrocarbon would be a function of the composition of the solution and hence the hydrocarbon halide yield would not be composition independent. The fact that this assumption must apply when the solution contains only about one part in ten to twenty of hydrocarbon should, in principle, yield the information necessary for a calculation of the width of the energy interval in which the reaction can occur, because each active chlorine atom must make a sufficient number of collisions in this energy interval to encounter a hydrocarbon molecule at least once. However, in view of the very approximate nature of the assumptions involved, we have not felt it profitable to make the calculation.

Thus the initial rapid decrease in yield of active carbon tetrachloride is qualitatively explained because small quantities of the hydrocarbon insure reaction with the active chlorine atoms before they have lost enough energy to exchange effectively with carbon tetrachloride; and hence some of the active chlorine atoms are made unavailable for the exchange reaction with carbon tetrachloride. This would suggest that after an allowance is made for the active chlorine atoms which react with the hydrocarbon, the intrinsic composition dependence of the yield of carbon tetrachloride, as predicted by the physical impact theory, might exhibit itself more clearly. This eventuality is manifest in Figs. 5 and 6 which show the measured carbon tetrachloride yields and predicted curves for the dependence of yield on mole fraction for the cyclohexane and benzene systems respectively. These curves were calculated by assuming that:

(1) Every radioactive recoil atom forms an excited intermediate complex with the hydrocarbon diluent (except for very small concentrations of benzene in carbon tetrachloride, when the probability of this is less than unity and is evaluated from the data).

(2) This complex can decompose by any of at least four reaction paths, each path characterized by a definite probability which is independent of the composition of the system. Products of these paths are, respectively, chlorine substituted hydrocarbon, the lower boiling active component found with carbon tetrachloride, free active chlorine atoms (which can subsequently exchange with carbon tetrachloride by the impact mechanism), an extractable compound of chlorine which does not exchange with carbon tetrachloride (possibly hydrogen chloride).

The values of p appropriate to given values of N were calculated from bond radii.[16] The probability of decomposition into cyclohexylchloride, or chlorobenzene, was obtained from the composition-independent value of yield of this substance. That for decomposition into lower boiling active compounds was estimated from the fractional distillation data. The probability of the process which gives extractable but non-exchanging species was not independently measured, but was arbitrarily chosen for best fit. (These values were 0.63 for the

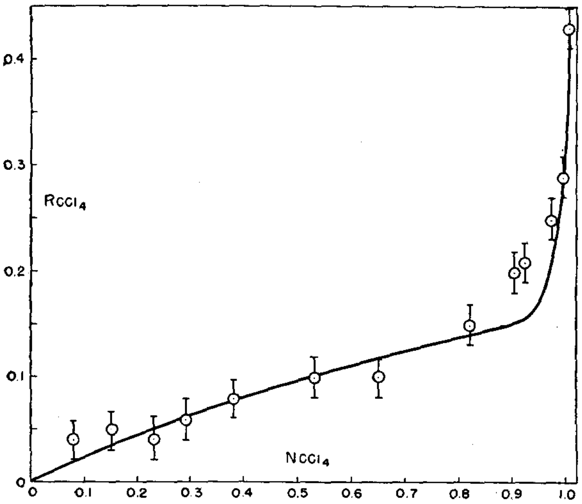

FIG. 6. A comparison of the yield of radioactive carbon tetrachloride as predicted by the physical impact theory (after allowing for the reactions with benzene) with the experimentally determined yield (after correcting for the lower boiling activity that is not carbon tetrachloride) in the carbon tetrachloride-benzene system.

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[16] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1942), p. 53.

cyclohexane system and 0.40 for the benzene system.) It is seen that the calculated curves can be well fitted to the measured points, except in the neighborhood of the sharp knee. This region will require further careful study.

Thus we see that when the special features of the reactions between the recoil atoms and hydrocarbon diluents are isolated, the substantial effects remaining are consonant with the physical impact theory. It is evident, however, that much further investigation will be necessary before its areas of applicability and its limitations can be established.

In view of the fact that it is necessary to account for reactions (e.g., hydrogen substitution) not provided for by the physical impact theory, and of the fact that the occurrence of these reactions casts doubt on a basic assumption (elastic atom-atom collisions) of this theory, it seems advisable to inquire whether the results which have been treated by it could be interpreted in terms of other ideas. Indeed, one can relinquish entirely the idea of elastic atom-atom collisions, and consider the intrinsic concentration dependence of the carbon tetrachloride retention exhibited in Figs. 5 and 6 to be the consequence of competing chemical reactions which occur in an energy range below that in which the radioactive hydrocarbon chloride is formed, but enough above thermal energy so that the usual temperature dependence of reactions will not appear.

A group of such competing reactions could be, for example,

$$\text{(A)}\quad Cl^*+CCl_4\rightarrow CCl_3Cl^*+Cl$$

$$\text{(B)}\quad Cl^*+CCl_4\rightarrow ClCl^*+CCl_3$$

$$\text{(C)}\quad Cl^*+RH\rightarrow HCl^*+R.$$

The experimental curves can be fitted by assigning relative cross sections for these reactions. (These cross sections are not necessarily those which would be inferred from the temperature independent term of the conventional absolute reaction rate expressions for each reaction of this set.) The relative cross sections will differ from those assumed for the above calculation of p from N. They no longer refer only to the probability of impact, but also include the probability that a specified reaction occurs. They are thus analogous to cross sections for nuclear processes. If it is assumed that all the active chlorine atoms react either with the hydrocarbon in the higher energy range to form active hydrocarbon chloride (or the other species previously mentioned) or in the manner given in reactions A–C, the relative cross sections of the reactions A:B:C are in the ratio of 1:1.3:11 for carbon tetrachloride-benzene, and 1:1.3:14.4 for carbon tetrachloride-cyclohexane. If, on the other hand, not all of the active chlorine atoms react before attaining thermal equilibrium, a more detailed analysis can be carried out which involves the impact cross sections of the reacting species, the probability of a reaction in a collision of the appropriate kind, and the average number of collisions made by a radioactive chlorine atom in the reactive energy range. Such a calculation cannot yield unique values of these parameters with the data at hand and will not be presented here.

The latter interpretation can also be applied to the observed carbon tetrachloride yield in the carbon tetrachloride-silicon tetrachloride system. The similarity of carbon tetrachloride and silicon tetrachloride would tend to make their relative effectiveness in these kinds of competing reactions depend only upon their relative concentration, and further would tend to make the respective energy ranges in which they could react with chlorine atoms very nearly alike. The proportionality between yield and mole fraction would thus be qualitatively accounted for.

With respect to the systems containing dissolved chlorine the following may be added to the remarks which appear in the presentation of the results. Since the chlorine atoms which survive reaction with hydrocarbon must ultimately find themselves in water extractable form after cooling to thermal energy, competition between reactions analogous to A, B, and C does not affect the over-all retention. Further, since an experimental method for differentiating among the various forms of extractable activity has not yet been devised, it is not at present possible to give numerical specification to the reaction cross sections of the competing processes in which the atoms that have escaped hydrocarbon chloride formation may be involved. The observation that the presence of chlorine dissolved in benzene has an effect upon the fate of the hot atoms that is consistent with photo-chemical results serves to emphasize the fact that ordinary, as well as extraordinary, reactions must be considered in a discussion of "hot atom" chemistry.

In the foregoing discussion it was stated that the addition of small quantities of hydrocarbon would have little, if any, effect upon p or $W(E)$ of Eq. (1). In this connection, two possible ways in which $W(E)$ could be affected by the addition of hydrocarbon without change in the basic assumptions of the physical impact model should be considered. The first of these is suggested by the interpretation Lu and Sugden[2c] gave for the rapid decrease in retention consequent to the addition of aniline; i.e., a newly formed radioactive carbon tetrachloride molecule, before dissipating its excess energy to the walls of the liquid cage, may react with a hydrocarbon molecule in the wall of the cage to give either stable active carbon tetrachloride, active hydrogen chloride, or active hydrocarbon chloride. The resultant abrupt reduction in $W(E)$ would explain the rapid decrease in the carbon tetrachloride yield and would, indeed, predict the rapid increase in hydrocarbon chloride yield. However, it would also predict that the hydrocarbon chloride yield would be composition dependent, since the yield of its precursor depends on the composition. This is clearly in disagreement with the experimental results. The second manner in which $W(E)$ might be rapidly decreased by the addition of small amounts of hydrocarbon arises from the result of the physical impact theory that the yield of radioactive carbon tetrachloride is proportional to the minimum energy required to escape a liquid cage.[8,9] Thus if the addition of a small quantity of hydrocarbon caused a large decrease in this parameter, the yield would be abruptly lowered. However, this does not lead to any reasonable picture of the way in which hydrocarbon chloride is formed in constant yield.

CONCLUSIONS

The chemical reactions of radioactive recoil chlorine atoms formed by neutron capture observed in this investigation are reactions which lead to the formation of chemically stable compounds containing the radioactive chlorine. The results indicate that these reactions occur predominantly with chlorine atoms which have lost most of their original kinetic energy but have not yet been reduced to the thermal range. This conclusion is drawn from comparison of the yields of radioactive carbon tetrachloride and of hydrocarbon chloride. For, the energy of the chlorine atom which forms the latter product must not be very large, else the result would not simply be the replacement of a hydrogen by a chlorine, but rather the carbon skeleton would be splintered and there would be a large variety of active organic products. On the other hand, the exchange reaction with carbon tetrachloride, which can in principle occur at the high initial energy but not with appreciable probability at thermal, appears to occur at a lower energy than the substitution reaction with hydrocarbon.

The consistency between the data and calculations based on the physical impact theory indicates that this theory may be useful in predicting the behavior of other systems. However, in order to achieve this consistency it was necessary to supplement the theory by considerations not contained in it. It is therefore evident that this approach does not in itself suffice to describe the chemical reactions of recoil atoms.

A more accurate description of these processes is probably to be formulated in terms of a more familiar chemical approach to the various reactions which are observed. Such an approach must allow for the fact that the reactions occur at energies governed by the slowing down process. This energy distribution will have a profound effect upon the competition among the various possible reactions.

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The Study of Restricted Rotation by Gas Diffraction

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A probability function has been derived which characterizes the variation of an interatomic distance affected by the restricted internal rotation of a molecule. The probability function takes into account the general vibration of the molecular frame in addition to the internal libration. The theory and practice are developed for determining the values of the parameters in the probability function directly from experiment. In addition the contribution from this probability distribution to the intensity of electron scattering is derived.

THE study of the scattering patterns of molecules which undergo restricted internal rotation affords a method for investigating this motion. Previous theoretical studies have been made of the intensity patterns for molecules undergoing internal torsions.[1,2] In these investigations the torsional oscillation was treated as a separate entity and the additional effect of the over-all vibration of the molecular frame was neglected. Recent developments in the technique for obtaining quantitative diffraction data and their theoretical interpretation[3] permit a detailed study of internal motion in molecules. It is therefore desirable to develop a restricted rotation theory which includes the effects not only of the torsional oscillation but also the general vibration of the molecular frame.

The general theory of the effect of small vibrational motion on scattering by gas molecules has been developed by R. W. James[4] which shows that, to a very good approximation, the contribution of the general vibration of the molecule to the probability function describing an interatomic distance is of Gaussian form. In this paper a theory of the effect of internal rotation on scattering by gases is developed in which the probability function describing the variation in interatomic distance (for distances that vary with the torsional oscillation) is given in terms of two independent contributions. One is the contribution of the restricted rotation based upon the quadratic form of the potential barrier at small angles, and the other is a Gaussian contribution as suggested by the theory of James.[4]

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[1] P. Debye, J. Chem. Phys. 9, 55 (1941).
[2] J. Karle, J. Chem. Phys. 15, 202 (1947).
[3] I. L. Karle and J. Karle, J. Chem. Phys. 17, 1052 (1949).
[4] R. W. James, Physik. Zeits. 33, 737 (1932).