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The Relative Rates of Reaction of Hydrogen and Tritium Hydride with Chlorine*

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The ratio of the specific rate constant for H_2 to that for HT in the photo-chemical reaction with chlorine has been determined at four temperatures and is represented by $R=(1.35\pm0.03)\exp\{(552\pm7)/RT\}$ to within about 0.3 percent. The ratio is found to be the same when the reaction is initiated by the tritium β-particles. The data are considered from the viewpoint of the theory of absolute reaction rates.

INTRODUCTION

THE relative rates of reaction of species differing only in isotopic constitution are of considerable practical interest, particularly in connection with isotope enrichment, and of theoretical interest as well, in the testing of theories of reaction kinetics. The relatively large differences in kinetic behavior exhibited by the isotopes of hydrogen should make relative rate studies involving tritium a worthwhile supplement to corresponding data obtained with deuterium.

Rollefson[1] has measured the relative rates of photochemical reaction of hydrogen and deuterium with chlorine at 0°C and 32°C by comparing the rate of each isotope with that of carbon monoxide. Farkas and Farkas[2] studied the photo-chemical reaction of chlorine with a mixture of hydrogen and deuterium in which the latter was present principally as deuterium hydride. In the present work the relative rates of reaction of hydrogen and tritium hydride were determined.

The chain mechanism of Nernst is generally accepted for the reaction between hydrogen and chlorine, in which the principal steps of interest here are (1) and (1′):†

$$H_2+Cl\xrightarrow{k_1}HCl+H \tag{1}$$

$$H+Cl_2\rightarrow HCl+Cl. \tag{1′}$$

Step (1) is the rate determining step, involving an activation energy of about 6000 cal, while (1′) is much faster.

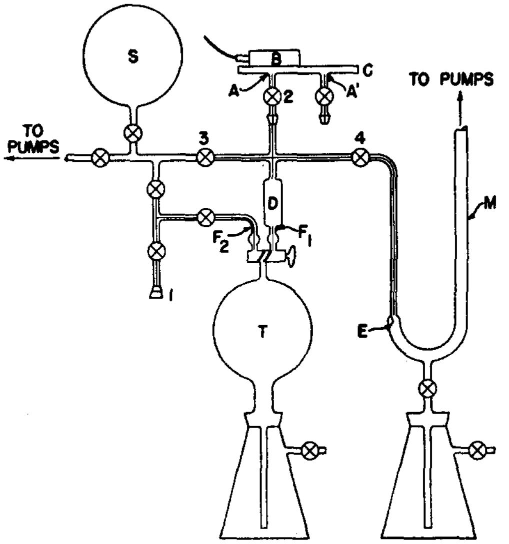

FIG. 1. Gas measurement and transfer system.

In the HT reaction step (1) has two counterparts:

$$HT+Cl\xrightarrow{k_{2a}}H+TCl \tag{2a}$$

$$HT+Cl\xrightarrow{k_{2b}}T+HCl. \tag{2b}$$

In the present work the relative rates of (1) and the sum of (2a) and (2b) were compared; that is, $R=k_1/k_2$ was determined, in which $k_2=k_{2a}+k_{2b}$.

For the case of measurement of the relative rates in the same reaction vessel we may write from Eq. (1) and Eqs. (2a) and (2b):

$$\frac{-d(H_2)}{dt}=k_1(Cl)(H_2) \quad\text{and}\quad \frac{-d(HT)}{dt}=k_2(Cl)(HT)$$

whence

$$R=k_1/k_2=\log[(H_2)_i/(H_2)_f]/\log[(HT)_i/(HT)_f] \tag{3}$$

in which i and f refer to the initial conditions and to the final conditions after the reaction has been carried to the desired degree of completion. It is thus seen that the relative rates are independent of the chain carrier concentrations and thus of the small and variable amounts of impurities which, by introducing chain breaking steps, make reproducibility very difficult in absolute rate measurements. Such impurities are normally present in such small amounts as to react with but a negligible fraction of the hydrogen.

EXPERIMENTAL

The experimental method may be understood from the discussion below with reference to Fig. 1.

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* This paper is based on work performed under University of California Contract with the AEC.

[1] G. K. Rollefson, J. Chem. Phys. 2, 144 (1934).

[2] L. Farkas and A. Farkas, Naturwiss. 22, 218 (1934).

† For a general discussion and survey of this reaction reference may be made to W. A. Noyes and P. A. Leighton, *The Photochemistry of Gases* (Reinhold Publishing Corporation, New York, 1941).

A mixture of hydrogen and tritium, sufficiently dilute in the latter so as to insure its presence almost entirely as HT, is allowed to react with chlorine, either under the influence of light or in the dark under the influence of the tritium β-radiation. The hydrogen is determined by pressure measurements, and the tritium is determined by the counting of the x-rays emitted from a small cell, provided with a thin metal window and containing some of the hydrogen-tritium hydride gas. The pressure and counting data, determined before and after reaction, are used, along with certain corrections mentioned later, to compute R from (3). Details are discussed below.

Initially, mercury filled the Toepler pump T of one-liter volume and extended up to the fiducial mark F_1 on a section of capillary tubing. Counting cell A', identical to the fixed cell A and used to monitor the behavior of the counting equipment over the time of experiment, was provided with a standard taper and was initially attached at joint 1. The system was brought to a high vacuum with a mercury diffusion pump, and a mixture of H_2-HT was admitted from bulb S so as to fill cells A and A' and volume D of about 100-cc capacity to the desired pressure. The mercury in the manometer M was brought up to a definite position E, defined by a teat of cobalt glass. Uniform temperature over the region containing gas was attained with a large fan. Temperatures were read at D and A with two mercury thermometers, graduated in 0.02°C intervals and calibrated against a standard platinum resistance thermometer. The pressure was read on the manometer M, constructed of 1-in. i.d. Trubore tubing, with a cathetometer, estimates of the meniscus positions being made to 0.001 cm. The valves to A and A' and the stopcock 3 were then closed, A' was transferred to its position on the counting block C, and the counting of A and A' with counter B was commenced. The cylindrical Pyrex reaction vessel was then attached at joint 1. The reactor was 55 mm o.d., had a volume of 200 cc, and was provided with a stopcock, separated from the main volume by a section of 1-mm capillary tubing so as to permit immersion in a bath. The reactor already contained the appropriate amount of chlorine, frozen down with liquid nitrogen. The gas bounded by 2, 3, F_1, and E was then transferred with T to the reactor. On the final transfer the mercury was raised to fiducial mark F_2. Knowledge of the volume between F_2 and the reactor stopcock allowed a correction for the gas not transferred to the reactor. The reactor was then transferred to the constant temperature medium. If the reaction was to be induced by light, time was allowed for temperature equilibrium to be attained before the reactor was exposed to the A-H6 mercury vapor lamp which was located at a suitable distance. The time for reaching temperature equilibrium was shortened by appropriate preliminary adjustment of the water bath when it was used as the constant temperature medium. Light passed through the surrounding bath and entered the reactor from the side. In some of the experiments the reactor was backed by a curved reflector of sheet aluminum in order to provide more uniform illumination. This had no apparent effect. The time of reaction varied from twenty minutes to several hours for the photo-chemical experiments. Times were longer for some of the β-particle-induced reactions. For a given value of R there is an optimum extent of reaction for which R is subject to minimum fractional error (see Appendix). For the present experiments it was desirable to carry the reaction to about 90 percent completion. Unfortunately the sensitivity of the reaction frequently did not allow this situation to be realized. After the reaction had progressed to what was estimated to be the proper extent, the reactor was removed from the bath, the chlorine and hydrogen chloride were frozen out with liquid nitrogen, and the unreacted hydrogen was transferred back into the volume bounded by 2, 3, F_1, and E. Meanwhile, the counting of the gas in A had been completed, the contents of A removed, and valve 2 closed. The pressure and temperature of the unreacted gas were determined, valve 2 was opened and inert H_2 was added until the gas had very nearly the same density as had prevailed in the measurement of the gas before reaction. This was done to eliminate the correction for different amounts of self-absorption in the counting of the gas before and after reaction. The gas was thoroughly mixed by alternate lowering and raising of the Toepler pump according to a schedule demonstrated to provide adequate mixing. When the system was at uniform temperature, with valve 2 open and with the mercury-gas interfaces at F_1 and at E, the pressure was measured. This measurement was made to verify that cancellation of the self-absorption corrections was assured and, in one case, to allow for such a correction. Valve 2 was then closed and the counting of A and A' was commenced. A correction, in addition to those already mentioned, must be made to the counting data of A to allow for the fact that after reaction A contains a different fraction of the total active gas than was the case before reaction. This correction is due to the different volumes involved, amounts to an average correction of 2.3 percent in R, and can be made with negligible uncertainty. It was also necessary to correct the pressure measurements for the HT and T_2 present, Corrections for the He^3 which grew from tritium decay subsequent to the preparation of the H_2-HT mixture were not needed. Correction was made to the counting data for the T_2 present, recognizing the twofold greater specific activity of T_2. For this calculation an approximate absolute value of the tritium content was needed, as well as the equilibrium constant for the equilibrium $H_2+T_2=2HT$. The gas composition will be mentioned later, and the equilibrium constant has the value 2.57.[3] It was estimated that the correction for the T_2 consumed in the reaction was negligible. It may be mentioned that the differing reaction rates cause

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[3] W. M. Jones, J. Chem. Phys. **16**, 1077 (1948).

the instantaneous distribution of H_2, T_2, and HT to differ from the equilibrium values. Errors could result if there were processes by which equilibration could be reached during the experiment. This does not seem very likely, however. In this connection Bonhoeffer and Harteck[4] have found that the ratio of orthohydrogen to parahydrogen is not altered toward the equilibrium value when gas enriched in parahydrogen is allowed to react partially with chlorine. Small corrections were made to both the pressure and counting data for the contents of the reactor stopcock, which did not undergo reaction. It was also assumed that half of the gas in the capillary section between the reactor stopcock and the main reactor volume behaved like the contents of the main reactor volume, while the remaining gas in the capillary did not react at all. This latter uncertainty amounts to about 0.07 percent in the final results and is much less than the over-all precision.

The pillbox-shaped sample cells A and A' were of brass and had $\frac{1}{8}$-in. bellows valves and standard taper joints. The cell volume was about 8 cc. The diameter of the cells was $1\frac{1}{2}$-in. and the cell end consisted of a network of $\frac{1}{8}$-in. holes so as to give about 50 percent transmission. A window of 0.0005-in. dural was waxed onto this grille with Apiezon W. The cells fitted snugly in holes in the bottom of a trough milled in the counting block C. The cells rested on a shoulder so that the cell windows were $\frac{1}{64}$-in. below the level of the trough, into which the counter B fitted closely. The counter B had a side window of 0.0005-in. dural, and its extreme positions in the trough, determined by stops, placed the counter and cell windows opposite each other. This arrangement provided for exact reproduction of geometry. The need for adjusting the gas density by addition of inert H_2 has been mentioned. Fortunately exact adjustment was not necessary, since the counting rate drops by only about 0.08 percent per mm. Hg pressure of inert H_2 added to an active mixture at 15 cm Hg pressure. The weak tritium β-particles cannot penetrate the dural windows, and the counting rate is due to the x-rays which are generated, mostly in the cell window, by the β-particles. The observed counting rate is only a small fraction of the disintegration rate in the sample cell, but counting rates of 200–400 counts per second are observed for cells with pressures of about 15 cm Hg of gas in which the tritium is present at 1–2 atomic percent. The counter was of the methane flow type and was operated in the proportional region. A scaling circuit was used in conjunction with the pulse amplifier. The counter was made by drilling out the center of a rectangular block and is a modification of that used by Prestwood and Wahl.[5] Small corrections for dead time losses and for background were made. The performance of the counting arrangement was quite satisfactory and was much superior to that of ordinary Geiger counters. In general the accuracy of the counting appeared to be governed by statistical uncertainties and usually corresponded to a probable error of about 0.2 percent. The same counter was used throughout the experiments described.

It was thought at the outset that the behavior of the counting apparatus should be monitored by the cell A', identical in construction to A and filled at the same time with active gas in order to present a similar spectrum to the counter. In practice corrections due to changes in the counting equipment over the time of an experiment were not warranted.

The experiments were performed at four different temperatures. At the lowest temperature the reactor was set in an unsilvered dewar vessel containing freely evaporating liquid ammonia. The temperature was measured during the reaction with a copper-constantan thermocouple fastened to the reactor and calibrated against the vapor pressure of ammonia.[6] The change in R occasioned by temperature variation due to different atmospheric pressures was negligible, and the temperature given in Table I is an average for the three experiments at this temperature. For the experiments at 0°C the same Dewar was used with an ice-water slush. Water was occasionally removed and ice added to maintain the temperature. In the experiments at 33.25°C and 70.75°C a water bath constant to 0.01°C was used. Temperatures were measured with a calibrated copper-constantan thermocouple. In the first series of experiments, the photo-chemical runs at 33.25°C, it was necessary to correct the values of R for the fact that the reacting gas was warmer than the bath due principally to the heat of reaction (Draper effect). The correction was about 1.5 percent in the worst case. The correction was made on the basis of a separate and similar experiment in which the pressure rise on illumination was observed on a manometer communicating with the reacting gas and protected from corrosion with pure H_2. This experiment allowed an evaluation of the heat transfer coefficient from the reacting mixture to the bath. The auxiliary experiment, since it measures the average temperature rise of the gas on illumination, may not properly estimate the correction insofar as the reaction does not occur uniformly throughout the reactor and insofar as the gas can maintain a temperature gradient. However, the agreement of the corrected values with the much slower β-particle induced runs at the same temperature probably indicates that the error in the correction is not serious. In all other runs the correction was small enough so that it did not have to be made. The warming up of the gas due to recombination of chlorine atoms (Budde effect) was found by the same method to be approximately that found by Kistiakowsky,[7] not more than about 0.1°C, and constitutes a negligible part of the correction.

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[4] K. F. Bonhoeffer and P. Harteck, Z. physik. Chem. **4B**, 113 (1929).

[5] R. J. Prestwood and A. C. Wahl, J. Am. Chem. Soc. **71**, 3137 (1949).

[6] R. Overstreet and W. F. Giauque, J. Am. Chem. Soc. **59**, 254 (1937).

[7] G. B. Kistiakowsky, J. Am. Chem. Soc. **51**, 1395 (1929).

Tank chlorine of the Ohio Chemical and Manufacturing Company was used. The first batch of gas was dried by passage over a one-meter column of P_2O_5, followed by bulb to bulb distillation in which a middle fraction was retained. The gas was then stored in a one-liter bulb provided with a freezing-out leg. Apiezon *N* (and later Apiezon *L*) stopcock grease was used. Subsequently the drying step was eliminated and the material was stored as a solid in a small bulb surrounded by liquid nitrogen until it was to be used. A considerable amount of time was lost, especially at first, because of the unpredictable behavior of the reactants. Except for the experiments at 33.25°C, in which a possible dependence of R on excess chlorine was looked for, it was not considered necessary to measure the chlorine pressure accurately. The pressure was read with a mercury manometer in which the limb exposed to chlorine was protected to some extent by a layer of oil. Pressures could be estimated to 1 to 2 mm mercury. In the experiments where a more accurate pressure was thought desirable the rough pressure was used in conjunction with an air buffer and another manometer. Care was taken to have the chlorine at higher pressure than the air on opening the stopcock between the two gases. By closing the reactor stopcock soon after pressure equalization and by using capillary tubing and a ballast volume, air was kept from the reactor, and the mercury was not appreciably corroded except after considerable use.

In preparing the mixture of hydrogen and tritium hydride it was desirable to have the tritium content in the range one to two percent since this concentration represented a reasonable compromise between counting rate and T_2 content. Appropriate pressures of enriched gas (about 40 percent T) and pure hydrogen, measured with a cathetometer, were added to the one-liter bulb *S*. The enriched gas was freed from He^3, the tritium decay product, by taking the tritium up in uranium and removing the remaining gas. The enriched and inert gases were purified by the decomposition of uranium hydride. The uranium was finely divided and had previously been outgassed at temperatures well above those required for the decomposition of the hydride. In the case of the enriched gas care was taken to evolve the gas completely from the uranium in order to avoid discrimination effects. The interior of the storage bulb had been coated with a thin mirror of palladium obtained by vacuum evaporation of ringlets of palladium wire from a tungsten filament. The total weight of palladium was 15 milligrams. The mirror was oxidized to an amber color in the annealing furnace. The bulb was then evacuated, about 2 cm Hg pressure of hydrogen added, and a flame was then brushed over the bulb, instantly restoring the metal. A surface of this sort should rapidly promote equilibrium among the diatomic molecules.[8, 9] As an added precaution the gas was allowed to stand for a week before use. No effects attributable to lack of attainment of equilibrium were observed over a time in which the tritium β-radiation should have established the equilibrium in the absence of a catalyst. The tritium content of the gas was obtained from the dilution data and the content of the enriched gas, which was originally based on gas density measurements. The calculated atomic percentages of tritium in the two preparations were found in this way

TABLE I.

T, °K	P_{Cl_2}, cm Hg at 25°C	P_{H_2+HT}, cm Hg at 25°C	Atomic fraction of T in initial gas	Time of reaction, hours	Fraction of H_2 consumed (approximate)	$R_{\text{corrected}}$
234.68	30.3	8.2	0.0148	8.7	0.75	4.40
	29.7	8.9	0.0148	9.8	0.90	4.43
	30.3	8.6	0.0148	10.0	0.89	4.43
						Av. 4.43±0.01
273.16	30.7	8.8	0.0148	6.9	0.84	3.73
	30.0	8.4	0.0148	4.8	0.79	3.67
	30.0	9.0	0.0148	8.0	0.97	3.72
	31.0	8.0	0.0194	116.	0.90	3.76*
	31.0	6.9	0.0194	14.1	0.84	3.71*
						Av. 3.72±0.02
306.41	15.56	7.1	0.0148	0.33	0.86	3.33
	30.10	9.0	0.0148	0.28	0.57	3.32
	30.93	9.5	0.0148	0.50	0.56	3.32
	29.09	9.3	0.0148	0.33	0.76	3.34
	31.2	7.3	0.0194	16.3	0.93	3.35*
	31.0	7.4	0.0194	16.3	0.94	3.35*
						Av. 3.33±0.01
343.91	26.5	5.4	0.0148	4.5	0.76	3.03*
	28.5	8.3	0.0148	8.0	0.85	3.05*
						Av. 3.04±0.01

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[8] H. W. Melville and E. K. Rideal, Proc. Roy. Soc. **153A**, 89 (1935).

[9] Beeck, Smith, and Wheeler, Proc. Roy. Soc. **A177**, 62 (1940).

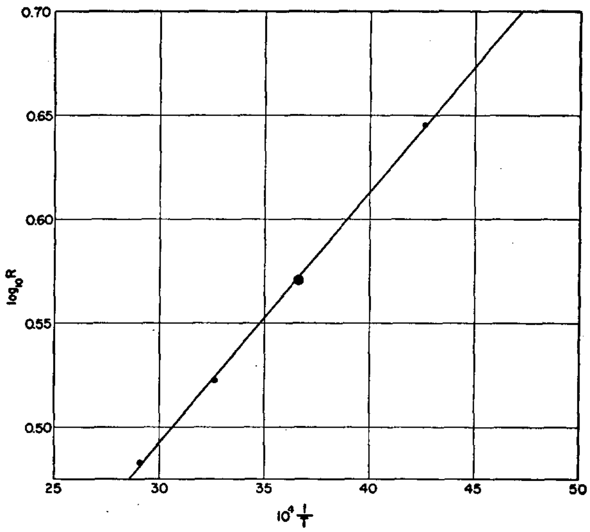

FIG. 2. Plot of experimental data.

to be 1.48 and 1.92 percent. As a check the composition of the second preparation relative to the first was determined by counting and was found to be 1.96 percent. The second sample was also analyzed on a mass spectrometer and found to contain 1.94 percent tritium. The error in R due to uncertainty in the tritium content should be less than 0.1 percent.

RESULTS AND DISCUSSION

The data are given in Table I. Columns two and three give the chlorine and total hydrogen pressures in the reactor at 25°C. Since the hydrogen pressure needs to be known accurately only in the measuring volume D, and since the ratio of this volume to the reactor volume is not known accurately, the pressures in column three are only approximate. Column seven gives the final values of R, including the several corrections mentioned. The uncertainty is the mean deviation.

It was thought that the value of R might depend slightly on the ratio of chlorine to the hydrogen chloride produced since these two species compete for atomic hydrogen in reaction (1′) and in the reverse of reaction (1). By altering concentrations and the extent of reaction in the experiments at 33.25°C the ratio of average chlorine to average hydrogen chloride concentrations was varied from 2.0 to 5.4. There was no apparent trend in R, and the effect is assumed absent at the other temperatures as well. For the conditions prevailing in these experiments, this result is in accord with the discussion of Potts and Rollefson,[10] who have studied the inhibitory effect of hydrogen chloride on the photo-chemical reaction between hydrogen and chlorine. The effect may well exist at low concentrations of chlorine. Indeed, the occurrence of the reverse of reaction (1) under such conditions has been suggested in connection with the relative rate experiments of Farkas and Farkas,[2] in which the consumption of hydrogen relative to that of deuterium was observed to fall as the reaction proceeded.

The starred values of R were obtained from experiments performed in the absence of light and initiated by the tritium β-particles. As can be seen there is no difference between these values of R and those obtained from the photochemical reactions.[11]

The values of $\log_{10} R$ are plotted against $1/T$ in Fig. 2, giving a linear relationship within experimental error. R is represented by $R = (1.35 \pm 0.03) \exp\{(552 \pm 7)/RT\}$. Thus the ratio of frequency factors is equal to the collision theory value of 1.38 within the experimental uncertainty, and the hydrogen reaction has the lower activation energy by 552 calories. The constants and their uncertainties, expressed as probable errors, were obtained by the method of least squares. The average deviation between the observed and computed values of R is about 0.3 percent.

We wish now to examine the data with a view to a possible difference in the activation energies of reactions (2a) and (2b), assuming that the Arrhenius equation may be applied. It is also assumed that (2a) and (2b) have equally effective collision numbers, and that the sum of these collision numbers is related to that for (1) by the collision theory.‡ If (2a) and (2b) have different activation energies, Q_{2a} and Q_{2b}, then a plot of $\log R$ against $1/T$ will not be a straight line, but would in the present case be concave down. If the experiments were performed at sufficiently low temperatures the slower reaction would be excluded, the apparent activation energy would approach the smaller of $Q_{2a} - Q_1$ and $Q_{2b} - Q_1$, while the apparent ratio of frequency factors would approach twice the value to be expected if Q_{2a} and Q_{2b} were equal. If the measurements were made at sufficiently high temperatures, the observed activation energy would approach $[(Q_{2a} - Q_1) + (Q_{2b} - Q_1)]/2$, and the frequency factor ratio would approach that expected for equal values of Q_{2a} and Q_{2b}. It may be seen from Fig. 2 that there is no evident tendency toward concavity. In addition the ratio of frequency factors obtained is not greater than the collision theory value. The data were treated from the viewpoint of the effect which a difference in Q_{2a} and Q_{2b} would have on the frequency factor ratio obtained. If it is granted that the experimental results exclude a frequency factor ratio greater than 1.39 (i.e., 0.01 unit greater than the collision theory value), then (2*a*) and (2*b*) cannot differ

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[10] J. C. Potts and G. K. Rollefson, J. Am. Chem. Soc. **57**, 1027 (1935).

[11] S. C. Lind, *The Chemical Effects of Alpha Particles and Electrons* (The Chemical Catalogue Company, Inc., New York, 1928).

‡ From the thermodynamic point of view of absolute rate theory the effect of the symmetry number two for hydrogen which occurs in the rotational partition function is to increase the concentration of the critical complex for hydrogen, so giving a larger reaction rate. From a kinetic point of view the effect is due, in the present linear model, to the two equivalent ends of the hydrogen at which chlorine may react. In the case of HT the symmetry number is one, but this is counteracted by the existence of two reactions, (2a) and (2b), each of which contributes to the removal of HT.

in activation energies by more than about 100 calories. If Q_{2a} and Q_{2b} are indeed different by about this amount, the observed difference in activation energies would then be quite closely the average difference indicated above. It is evident that this procedure is not a very sensitive one for determining a difference in Q_{2a} and Q_{2b}, and that this difference could be much larger if the actual situation were not that assumed. The "tunneling" phenomenon of absolute reaction rate theory, by giving opposite curvature to the relationship between $\log R$ and $1/T$, might, for example, influence the frequency factor ratio in such a manner as to conceal a difference in Q_{2a} and Q_{2b}. A direct search for a possible difference in (2a) and (2b) would be very desirable. Professor Rollefson has suggested that this might be possible if the experiment were carried out in the presence of sufficient oxygen and the splitting of the radioactivity between hydrogen chloride and water determined. The experimental difficulties of preventing exchange in such an experiment might be rather considerable, however.

In considering the question of reaction rates from the viewpoint of the theory of absolute reaction rates there may, at least in principle, be a distribution of intermediate complexes through which the reaction is regarded as passing, and the total rate will then be obtained by integration. In practice such a procedure would present a considerable amount of work, which would probably not be justified in view of the approximate methods employed in the construction of potential energy surfaces. In addition the variety of effective intermediate configurations will be greatly restricted by the exponential dependence of the rate constants on the energy of activation. It is therefore ordinarily assumed that the reaction proceeds through a single intermediate state.[12]

The semi-empirical method of the theory of absolute reaction rates has been applied to hydrogen-halogen reactions by Wheeler, Topley, and Eyring[13] (WTE). The critical complex was assumed for simplicity to have a linear HHCl structure. For the reaction between tritium hydride and atomic chlorine two complexes, HTCl and THCl, are then to be expected, and these might differ considerably in properties. Indeed, if the force constants and molecular dimensions obtained by WTE[13] are assumed, we obtain the ratios of rate constants for reactions (1), (2a), and (2b), which are given in Table III. The ratios were calculated utilizing Eq. (28) of WTE and take account of the "tunneling" effect. The molecular constants needed are given in Table II. The moment of inertia of the linear complex is I, the stretching frequency is ν_+, the imaginary frequency corresponding to motion along the direction of decomposition is ν_-, and the bending frequency is ν_ϕ. Frequencies were computed from the force constants given by WTE. The small differences of the values for HHCl from those of WTE are negligible.

TABLE II. Properties of complexes.

System	I, Molecular weight and Angstrom units	ν_ϕ cm^{-1}	ν_+ cm^{-1}	ν_- cm^{-1}
H−H−Cl	8.62	491	2489	716 i
H−T−Cl	11.33	334	1488	711 i
T−H−Cl	21.43	460	2485	426 i

Comparison of Tables I and III shows that the calculated ratios of rate constants are substantially smaller than those observed. Table III shows that there is a very large difference in the theoretical rates of (2a) and (2b). In addition reaction (1) has, on this theory, a higher activation energy than reaction (2a), causing the theoretical temperature coefficient of k_1/k_2 to differ even in sign from the experimental results (the temperature dependence of the frequency factor ratio is not large for the frequencies of Table II in the temperature range considered.) In computing the values of Table III it was found that the ratios of frequency factors were substantially larger than 1.35, the experimental value.

It was previously noted by WTE themselves that their calculations did not satisfactorily predict the relative reaction rates of hydrogen and deuterium with chlorine. The relative rates were found experimentally to be 13.4 and 9.75 at 0°C and 32°C, whereas the theoretical ratios are 5.4 and 4.7. The value of 3.3 at 32°C given by WTE appears to involve some error. Thus the theoretical values are low, although the activation energy is of the correct sign. The experiments of Farkas and Farkas[2] are open to some question, because of the presence of some D_2 and because the ratio of rate constants dropped as the reaction proceeded. If, however, we take the relative rates at the start of the reaction as a measure of the relative rates of H_2 and HD, this has the value 3.8 at 30°C, and the computed value of 2.2 is again low. Steiner and Rideal[14] studied the reaction rates between deuterium and hydrogen chloride and between hydrogen and deuterium chloride at 900°K, in which the slow steps were inverse to the steps which have so far been considered. At the higher temperatures the fractional difference in the relative rates is smaller. It was also necessary to correct for the simultaneous occurrence of a bimolecular reaction. Nevertheless Steiner and Rideal found that the dis-

TABLE III. Theoretical relative rates.

T, °K	k_1/k_{2a}	k_1/k_{2b}	k_1/k_2
234.68	0.99	35.3	0.96
273.16	1.19	26.2	1.14
343.91	1.47	16.2	1.29

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[12] J. L. Magee, J. Chem. Phys. 8, 677 (1940).

[13] A. Wheeler, B. Topley, and H. Eyring, J. Chem. Phys. 4, 178 (1936).

[14] H. Steiner and E. K. Rideal, Proc. Roy. Soc. **173A**, 503 (1939).

crepancy between experiment and the WTE theory was of the same sort as has been mentioned.

It is not easy to decide, granting the fundamental correctness of the absolute rate theory, whether the discrepancies which have been mentioned are due to the incorrectness of the model chosen or simply to the approximate nature of the calculations. It was suggested by WTE themselves that the disagreement of theory with the experimental absolute rate of reaction of hydrogen with chlorine and with the relative rates of hydrogen and deuterium could be attributed to too large frequencies computed for the intermediate state. The calculations lead to conclusions which seem to be even at qualitative variance with the most direct interpretation of the HT data, however, and the suggestion of Magee,[12] that the complex may be triangular, seems particularly inviting.

Magee investigated the effects of directed valence on reactions of this type, using the simple Heitler-London theory, and concluded that a triangular complex would be more stable than a linear complex, although the breakdown of the method at small separations made it difficult to draw conclusions regarding quantitative details. Magee also pointed out that the change from a linear to a triangular complex might bring the theory into better agreement with experiment. When a vibrational degree of freedom is replaced by one of rotation, the frequency factor is increased, while the zero point energy of the complex is decreased. Both of these effects increase the theoretical rate toward agreement with the experimental values for the absolute reaction rates of hydrogen with chlorine and bromine atoms (see reference 12, page 685).

The triangular complex, applied to the reactions of H_2, HT, and D_2 with chlorine, should also improve the computations on relative rates, both in regard to frequency factors and in regard to activation energies. The calculations on the linear model show that the ratios of the frequency factors, which are not very temperature dependent in the neighborhood of room temperature, are larger than the experimental values, while the computed differences in activation energies are too small. The latter circumstance is due to the too large zero point energies of the complexes. Replacing a vibrational degree of freedom by one of rotation, in passing from the linear to the triangular model, will increase the frequency factors for the H_2, HT, and D_2 reactions, but the effect will be greater for the heavy molecules (unless the frequency replaced is very low, in which case the mass dependence disappears), and the ratio of frequency factors will be lowered in the direction of the experimental values. The comments in this connection of Glasstone, Laidler, and Eyring at the top of page 226 of their book[15] do not appear to be correct. The removal of a vibrational frequency will increase the difference in activation energies and, in particular, acts to eliminate the anomalous temperature dependence of Table III. The effect on the activation energy, since this quantity occurs in an exponential, would be expected to override the decreased ratio of frequency factors so that the triangular model should increase, relatively, the rate of the light hydrogen isotope. A triangular model would also decrease the large difference in the rates of (2a) and (2b) given in Table III.

It must be admitted that the arguments reviewed above rest on a rather insecure foundation. A further theoretical study of the triangular complexes might be worthwhile.

Finally we wish to recall that in the relative rate calculations mentioned it has been assumed that the transmission coefficients are the same for the isotopic reactions. The considerations of Hirschfelder and Wigner[16] and of Hulbert and Hirschfelder[17] show that this may not be so. Unfortunately such calculations depend on a detailed knowledge of the potential energy surface in the neighborhood of the activated state which is not at present available.

I thank Professor G. K. Rollefson and Dr. T. W. Newton for their interest and suggestions.

APPENDIX

(*A*) Given two counting rates A_1 and A_2. It is desired to divide a total counting time T between the determination of A_1 and A_2 in such a way that A_1/A_2 is known with maximum fractional accuracy.

Let the times devoted to the determination of A_1 and A_2 be t_1 and $t_2=T-t_1$. Then the mean square fractional errors in A_1 and A_2 are $(A_1t_1)^{-1}$ and $A_2^{-1}(T-t_1)^{-1}$, and $(A_1t_1)^{-1}+A_2^{-1}(T-t_1)^{-1}$, the mean square fractional error in A_1/A_2, is at a minimum when

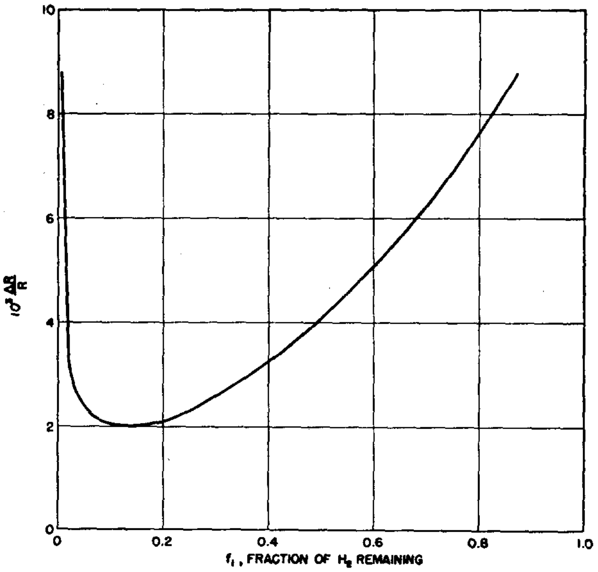

FIG. 3. Fractional error in R as function of extent to which reaction is carried.

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[15] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, New York, 1941).

[16] J. O. Hirschfelder and E. Wigner, J. Chem. Phys. **7**, 616 (1939).

[17] H. M. Hulbert and J. O. Hirschfelder, J. Chem. Phys. **11**, 276 (1943).

$t_1/T-t_1=(A_2/A_1)^{\frac{1}{2}}$, i.e., the times spent are inversely proportional to the square roots of the counting rates.

(B) In Eq. (3) suppose that each pressure measurement is considered to be subject to a constant error, a, and that the fraction of the initial hydrogen remaining at the end of reaction is f_1. If $\alpha=\ln[(H_2)_i/(H_2)_f]$, then it follows from standard error theory that

$$\left(\frac{\Delta\alpha}{\alpha}\right)^2=\left(\frac{a}{P_1}\right)^2\cdot\left(1+\frac{1}{f_1^2}\right)\Big/\ln^2 f_1, \tag{1B}$$

in which $(\Delta\alpha/\alpha)^2$ is the mean square error in α and P_1 is the initial pressure. Incidentally, the fractional error in (1B) above is at a minimum for $f=0.32$.

In Eq. (3), suppose that the initial corrected counting rate due to HT is A_1 and that at the end of the experiment the activity has dropped to $A_2=f_2A_1$, where f_1 and f_2 are related by $R=\ln f_1/\ln f_2$. Then it may be shown that the mean square error in $\beta=\ln f_2$ is given by

$$\left(\frac{\Delta\beta}{\beta}\right)^2=\left(\frac{1}{A_1t_1}+\frac{1}{f_2A_1}\cdot\frac{1}{T-t_1}\right)\Big/\ln^2 f_2. \tag{2B}$$

If the time t_1 is chosen according to (A) for minimum fractional error in β, Eq. (2B) becomes

$$\left(\frac{\Delta\beta}{\beta}\right)^2=\frac{[1+f_2^{\frac{1}{2}}]^2}{f_2A_1T\ln^2 f_2}, \tag{3B}$$

which is at a minimum for $f_2=0.08$.

The mean square error in R is given by

$$(\Delta R/R)^2=(\Delta\alpha/\alpha)^2+(\Delta\beta/\beta)^2. \tag{4B}$$

If the root mean square error in R is calculated from (4B) as a function of f_1 for the circumstances of the present experiments, there is a minimum in the neighborhood of $f_1=0.9$. Figure 3 shows this error as a function of f_1 for $P_1=15$ cm Hg, $a=0.005$ cm Hg, $A_1=200$ counts/sec, $T=4$ hours, and $R=3$. The steep rise near complete reaction is due principally to error in the measurement of the final pressure. Calculations of this sort serve as a useful guide even though the precision of the experimental data is affected by factors in addition to those considered here. Similar considerations have been applied to the kinetics of exchange reactions involving radioactive isotopes.[18]

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[18] N. Davidson and J. H. Sullivan, J. Am. Chem. Soc. **71**, 739 (1949).

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The Rate Constant of Ethane Formation from Methyl Radicals

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The rotating sector technique has been applied to a determination of the rate constant of methyl radical recombination in the photo-decompositions of acetone and mercury dimethyl, using the small but accurately measurable rate of methane formation as a measure of methyl steady-state concentration. The resulting value of the recombination rate constant is 4.5×10^{13} (moles/cc)$^{-1}$ sec^{-1}, with an activation energy of $E=0\pm700$ cal regardless of radical source. The determination of this constant permits the evaluation of the rate constants for several other reactions of methyl radicals. It is found that hydrogen abstractions have steric factors of the order of 10^{-4}.

THE absolute rates of elementary reactions in the gas phase are known with certainty for only a very limited number of such processes, although quotients and ratios of rate constants may often be found with some accuracy. The recombination of methyl radicals

$$CH_3+CH_3\rightarrow C_2H_6;\quad R_{C_2H_6}=k_1.(CH_3)^2 \tag{1}$$

is important in this respect, since a knowledge of k_1 permits the evaluation of many other reactions involving methyl radicals.[1,2] Reaction (1) is also of considerable intrinsic interest, since it represents an association of radicals neither as simple as single atoms, nor so complex as to provide enough parameters to fit any theory.

Previous quantitative work on this reaction seems confined to that of Allen and Bawn[3] and recently Marcus and Steacie.[4] A discussion of earlier, largely qualitative work is given by Steacie.[5] Allen and Bawn used Polanyi flame technique and were able to estimate only an upper limit for the collision efficiency of Eq. (1), which they believed to be $\frac{1}{10}$ or less under their conditions. Marcus and Steacie compared the rate of the reaction,

$$CH_3+NO\rightarrow CH_3NO;\quad -R_{CH_3}=k_2.(CH_3).(NO) \tag{2}$$

with that of Eq. (1) and found $k_2/k_1^{\frac{1}{2}}=2.8\times10^3$ (moles/cc)$^{-\frac{1}{2}}$ sec$^{-\frac{1}{2}}$. Using Forsyth's[6] value for the steric factor of Eq. (2), $s_2=1.4\times10^{-5}$, they concluded that reaction (1) had a steric factor $s_1=5\times10^{-3}$. Forsyth's value of s_2 is based on mirror removal experiments in a flow system, under conditions such that radicals (produced by pyrolysis of dimethyl ether) seemed to disappear by a first-order wall reaction. It is doubtful whether his results indicate anything other than a surface recombination, or possibly a poisoning of mirrors by NO. Any

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[1] A. F. Trotman-Dickenson and E. W. R. Steacie, J. Am. Chem. Soc. **72**, 2310 (1950).

[2] L. M. Dorfman and R. Gomer, Chem. Rev. **46**, 499 (1950). This paper contains references to pertinent work on acetone and mercury dimethyl photo-chemistry.

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[4] R. A. Marcus and E. W. R. Steacie, Z. Naturforsch. **4a**, 332 (1949).

[5] E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946).

[6] J. S. A. Forsyth, Trans. Faraday Soc. **37**, 312 (1941).