JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

(Registered in U. S. Patent Office) (© Copyright, 1960, by the American Chemical Society)

VOLUME 82 JUNE 16, 1960 NUMBER 11

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION NO. 1564, STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, NEW HAVEN, CONNECTICUT]

The Effect of Moderators on the Reactions of Hot Hydrogen Atoms with Methane

BY PEDER J. ESTRUP[1] AND RICHARD WOLFGANG

RECEIVED JULY 23, 1959

The reaction of recoil tritium with methane has been examined in further detail. The previous hypothesis that this system involves a hot displacement reaction of high kinetic energy hydrogen to give CH_3T, $CH_2T\cdot$ and HT is confirmed. The effect of moderator on this process is studied by the addition of noble gases. As predicted these gases inhibit the hot reaction, their efficiency in this respect being He > Ne > A > Xe. The data are quantitatively in accord with a theory of hot atom kinetics. The mechanism of the hot displacement process is briefly discussed.

Introduction

The reactions of gaseous methane with high kinetic energy hydrogen atoms—produced in the form of tritium (T) by the nuclear process $He^3(n,p)T$—has been the subject of several recent studies.[2-5] This Laboratory has postulated that the majority of the tritium atoms by virtue of their high energy undergo "hot" displacement reactions to form HT, CH_3T and $CH_2T\cdot$. The remainder, about 30%, of the tritium loses energy in collisions without combination and then undergoes relatively slow thermal reactions. These reactions are mainly abstraction of H from CH_4 to form HT, and combination with radiation produced species to form higher tritiated hydrocarbons.

In support of this hypothesis the following evidence was cited:

(1) The formation of hot products is unaffected by the addition of small concentrations of radical (and ion) scavengers such as I_2 while the thermal products are almost eliminated. Insensitivity of hot processes to minor concentrations of scavenger is expected since, if they occur at all, they must do so in a relatively few collisions before losing their excess energy.

(2) The hot products appeared to be insensitive to temperature, in accord with the expectation that the required energy is supplied by the hot atom.

(3) In a preliminary finding it was reported that the yields of hot products were sharply reduced by the presence of excess helium, a substance acting as a moderator in the sense of removing the excess kinetic energy of the hot atom.

The alternative suggestion that the reaction of recoil tritium actually involved T^+ rather than atoms did not conform to the results and can also be rejected on the basis of independent evidence.

The present paper reports on a more detailed study of the hot reactions occurring in this system; a study made in order to confirm and add detail to the reaction model postulated and to provide quantitative data to test the theory of hot atomic kinetics set forth in the accompanying paper.[6] The effect of the addition of various amounts of He, Ne, Ar and Xe as progressively less efficient moderators has been investigated. Further information has also been obtained on the effect of scavenger and temperature and on the fate of thermalized hot atoms.

Experimental

The experimental procedure has previously been described.[2] Samples containing He^3, methane and various additives were irradiated in the Brookhaven reactor and the resulting products subsequently analyzed by gas chromatography. The irradiation time was short, usually a few minutes, with a neutron flux of 10^{12}-10^{13} n./cm.^{2} sec. A number of samples were cooled during irradiation. Here the quartz ampoules were placed in polystyrene containers, which were then filled with an appropriate organic liquid.

---

[1] CERN, Geneva, Switzerland. Work performed in partial fulfillment of the requirements for the Ph.D. degree at Yale University.

[2] M. Amr. El-Sayed, P. J. Estrup and R. Wolfgang, *J. Phys. Chem.*, **62**, 1356 (1958).

[3] M. Amr. El-Sayed and R. Wolfgang, THIS JOURNAL, **79**, 3286 (1957).

[4] A. Gordus, M. Sauer and J. Willard, *ibid.*, **79**, 3284 (1957).

[5] M. Amr. El-Sayed, Ph.D. Thesis, Florida State University (1959).

[6] P. J. Estrup and R. Wolfgang, THIS JOURNAL, **82**, 2665 (1960).

The assembly was frozen and injected into the pile when the compound began to re-melt. The melting process kept the samples at approximately constant temperature for the short irradiation time. In this manner the temperature of samples could be varied from −100° to room (pile) temperature.

After irradiation the samples were, in general, stored in Dry Ice.

Effect of Scavengers.—Iodine, bromine and nitric oxide were used as scavengers. Excess of the halogens were added to the samples (in form of a crystal or a droplet) and their vapor pressure determined by control of the temperature during irradiation.

The results are shown in Table I, in which the yields of the various products are given as function of the pressure of scavenger P_s. The yields are given by the ratio between the observed activity A_i and the total available activity, A_s (see below).

TABLE I

REACTIONS OF RECOIL TRITIUM WITH METHANE

EFFECT OF SCAVENGERS

Scavenger	Temp.	P_s, mm.	$\frac{A_{HT}}{A_s}$	$\frac{A_{CH_3T}}{A_s}$	$\frac{A_{CH_2TX}}{A_s}$	$\frac{A_{Higher}}{A_s}$
..	≥Room	0	0.535	0.325	0	0.14
Br_2	~−100	~0.01	.42	.32	0.018	.11
Br_2	~− 60	~0.6	.37	.345	.042	.015
I_2	≥Room	~1	.35	.32	.020	< .01
Br_2	~− 45	1-2	.32	.36	.037	< .01
NO	≥Room	~ 9	.315	.365	...	< .01
Br_2	~−15	~20	.29	.33	.045	< .01
Br_2	≥Room	Large	.23	.30	.042	< .01

The large influence of very small amounts of scavenger is evident from this table. Higher hydrocarbons (*i.e.*, labeled ethane, propane, butane, etc.) essentially disappear at pressures larger than 1 mm. and at this pressure the yield of labeled methyl halide levels off to remain constant with increasing pressure of scavenger. The yield of labeled methane is seen to be unaffected by the scavenger within the experimental error. The yields of HT initially decreases sharply but for $P_s \leq 1$ mm. fall off very slowly. There are no indications that the scavengers used act with different efficiency.

"Saturation" then occurs quickly, namely, for $P_s \sim 1$ mm., which corresponds to a mole fraction of scavenger of about 0.001. The use of I_2 as scavenger with no cooling during irradiation then gives a satisfactory ($P_s \sim 1$ mm.) and convenient system.

Total Activity in the System.—The total activity A produced in a sample during irradiation can be calculated from a knowledge of the He^3 content, the irradiation time and the neutron flux. This activity is, however, invariably found to be larger than the experimentally observed activity, A_0 (in samples without scavenger). The discrepancy disappears when corrections are made for recoil and diffusion losses of tritium particles.

Some tritium is lost from the system because it is formed near the wall and recoils into it instead of being stopped in the gas phase. This recoil loss L depends on the recoil range of the tritons and of the dimensions of the ampoule. The calculation of L is discussed in appendix I. When corrections are made for such loss, we obtain A_s, the total activity available for reaction. Table II shows a comparison of calculated and experimental values for the activity in samples containing methane with no additives.

The activities are given in d.p.s. and the composition of the samples by the partial pressures of the compounds (in cm.). R is the diameter of the ampoule and r the recoil range of the tritons. The agreement between A_0 and A_s is good even for considerable variations of the dimensions of the ampoule and the total pressure.

TABLE II

COMPARISON OF EXPERIMENTAL AND CALCULATED ACTIVITIES

Composition P_{He^3}	Composition P_{CH_4}	A_0	A	R, mm.	r, mm.	L	A_s	$\frac{A_0}{A_s}$
2.9	110	54,000	65,000	5	1.66	0.175	53,700	1.00
2.8	95.5	20,100	37,500	2	1.90	.47	19,900	1.00
5.2	40.6	58,400	103,000	5	4.3	.43	58,800	0.99

For samples containing large amounts of moderator (*e.g.*, helium), it is necessary to correct also for those tritium atoms which become thermalized and diffuse to the wall before reacting in the gas phase. The magnitude of this diffusion loss is estimated in Appendix II on the assumption that the quartz walls of the ampoule act as a "scavenger" for diffusing (thermalized) tritium atoms. Table III shows a comparison between A_0/A_s and A_c/A_s, where A_c is the calculated activity with corrections for both recoil and diffusion losses. As seen the variations in the observed yield with helium concentration, with pressure, temperature and dimensions of the ampoule can be explained qualitatively by the corresponding changes in the diffusion loss. The quantitative agreement is actually somewhat better than expected.

TABLE III

COMPARISON OF OBSERVED AND CALCULATED ACTIVITIES; DIFFUSION LOSS INCLUDED

Composition P_{He}/P_{CH_4}	P_{total}, cm.	Temp., °C.	R, mm.	A_0/A_s	A_c/A_s
0	113	≥Room	5	100%	98%
26	101	≥Room	5	47	40
50	110	≥Room	5	29	32
0	46	≥Room	5	99	95
0	92	~−45	5	93	91
0	87	~−100	5	73	75
0	98	≥Room	2	100	95

It has been mentioned[2] previously that a temperature dependent re-entry of tritium from the walls can take place. This re-entry occurs not only during irradiation but continues until the sample is analyzed. This effect was eliminated by making the irradiation time short (1-2 min.) and by storing the samples in Dry Ice until they were analyzed.

Effect of Temperature, Pressure and Surface.—As seen above the changes in the total activity with variations of the temperature, pressure and dimensions of reaction vessel can be accounted for. The corresponding dependence of the thermal production of HT can be seen from the same considerations.

The yield of labeled methane, however, is unaffected by both temperature (see Table I) and pressure.[2] The production of labeled methyl radicals is observed only indirectly in the presence of I_2 or Br_2, and changes in the temperature are accompanied by changes in the halogen concentration. The effect was seen in Table I.

Changes in the dimensions of the ampoule gave the variations expected from calculations of recoil and diffusion losses. No effect was seen in the production of labeled methane or methyl halide.

Moderated Systems.—Some results for systems containing a moderating, noble gas are shown in Table IV and V. Helium was used most often but the effect of neon, argon and xenon also was investigated. In Figs. 1, 2 and 3 the yields of the various products are plotted against the mole fraction of methane, x, in the sample. Figure 4 shows a plot of the total yields of all observed products, A_0/A_1, for samples with scavenger. (The yield of labeled hydrogen halide is not included.)

The yields of HT are subject to error due to a side reaction which may become relatively important in highly moderated scavenged systems. Radiation will produce a small amount of hydrogen halide. This HX will react efficiently with thermalized tritium atoms to form HT. The amount of HX is sufficiently small so that only a small proportion of the thermalized tritium will react in this manner instead of with X_2. However, in highly moderated systems only 2% of the tritium may react hot to form HT and the yield of HT thus becomes very sensitive to this side reaction of the 98% thermal tritium. The increasing ratio of HT/CH_3T in scavenged and moderated systems probably is due to this spurious effect.

Discussion

The most striking feature of the formation of a product such as labeled methane is the independence the yield shows, to the presence of scavengers, to changes in temperature and pressure and to irradiation flux. A behavior of this kind can be under-

TABLE IV

IRRADIATION OF METHANE WITH TRITIUM. MODERATOR PRESENT

Composition			Moderator	Flux, n./cm.^{2} sec. × 10^{-12}	Irrad. time, min.	Yields in % of total activity obsd.				A_0/A_s
P_{He^3}	P_{CH_4}	P_{Mod}				H_2	CH_4	C_2H_6	High.	
2.6	62	96	He	12	2	74.1	24.7	0.9	0.3	0.91
2.7	13	112	He	12	2	65.0	21.0	12.2	1.8	.37
3.7	3.8	94	He	8	2.5	89.9	7.1	2.2	0.8	.47
2.3	2.2	105	He	12	2	83.9	7.7	6.5	1.9	.29
2.2	1.1	107	He	12	2	90.5	7.8	2.1	0	.20
2.7	12	107	A	12	2	51.8	42.0	7.6	2.6	.39
2.6	18	95	Xe	10	1.5	66.8	32.0	0.6	0.6	1.06

TABLE V

IRRADIATION OF METHANE WITH TRITIUM. MODERATOR AND I_2 PRESENT

Composition			Moderator	Flux, n./cm.^{2}, sec. × 10^{-12}	Irrad. time, min.	Yields in % of total activity obsd.						A_0/A_s
P_{He^3}	P_{CH_4}	P_{Mod}				H_2	CH_4	C_2H_6	Higher	CH_3X	EtX	
3.3	79	18	He	10	1.5	45.3	48.5	0.2	0.2	5.8	..	0.68
3.4	60	54	He	10	1.5	46.1	46.6	.5	.4	6.4	..	.636
3.3	31	65	He	10	1.5	48.4	44.6	.2	.3	6.5	..	.484
3.3	18	94	He	10	1.5	59.5	33.0	.5	.3	6.85	..	.315
3.1	5.0	105	He	10	1.5	65.0	26.8	.9	1.2	5.25	0.7	.117
2.3	2.3	105	He	12	2	71.8	24.2	..	..	4.0	..	.073
3.4	13	113	Ne	12	2	47.0	44.3	.1	0.1	8.7	..	.32
2.8	8.8	81	Ne	10	1.5	45.2	45.9	.2	0.8	7.9	..	.46

stood if it were formed by a hot reaction of the tritium atom. By contrast the higher hydrocarbons which are postulated to be formed by thermal reaction involving radiation produced species exhibit a complex dependence on these factors.

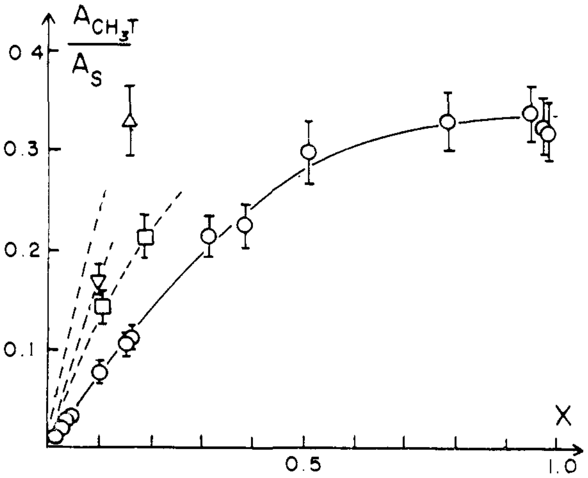

Fig. 1.—Plot of the relative yield of labeled methane as function of the mole fraction of methane; moderators: helium ○, neon □, argon▽, xenon △.

We may briefly examine some other mechanisms which might be advanced:

It has been suggested[4,7] that the reaction products were direct consequences of ion-molecule reactions. However, as mentioned, T^+ cannot be considered a probable reagent.[2] It is also doubtful whether T^0 will react with ions such as CH_4^+, CH_5^+ and CH_3^+. These species are most certainly formed during irradiation, but their density will be very small. It can be estimated that under the experimental conditions the steady-state concentration of ions is smaller than the methane concentration by a factor of 10^8. Furthermore, yields from ion-molecule reactions should be sensitive to the presence of a substance such as I_2, with a comparatively low ionization potential. However, as seen the yield of methane is not affected by I_2. Similarly, the yield in moderated systems is found to decrease in the series, Xe, A, Ne, He. The opposite behavior would be expected for ionic reactions. Thus, in studies on radiation induced exchange of T_2 and CH_4[8], Xe has a quenching effect attributable to its low ionization potential which permits it to discharge the reactive ions.[9]

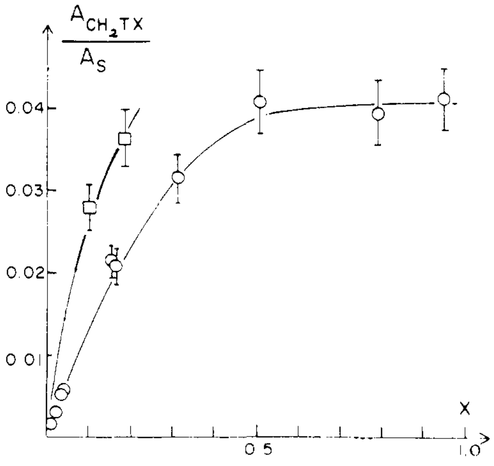

Fig. 2.—Plot of the relative yield of labeled methyl halide as function of the mole fraction of methane; scavenger present; moderators: helium ○, neon □.

---

(7) J. B. Evans, J. E. Quinlan, M. C. Sauer and J. E. Willard, *J. Phys. Chem.*, **62**, 1351 (1958).

(8) T. H. Pratt, Yale University, Ph.D. Thesis, 1960.

(9) In the present system it is interesting to note that the higher labeled hydrocarbons, which are formed by thermal reactions with radiation produced species, are sharply reduced by the Xe (see Table V). This is in accord with the explanation that the radiation produced species are themselves formed by processes involving ions.

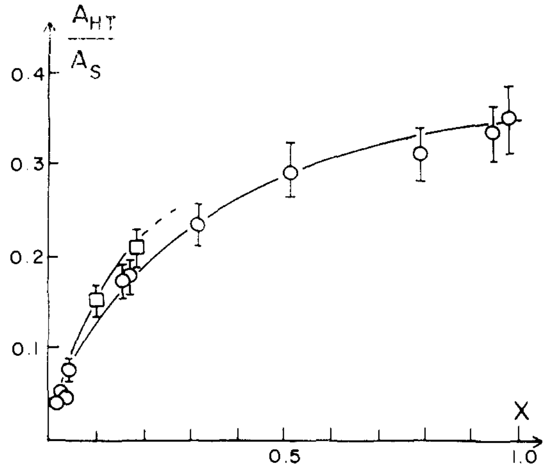

Fig. 3.—Plot of the relative yield of labeled hydrogen as function of the mole fraction of methane; scavenger present; moderators: helium ○, neon □.

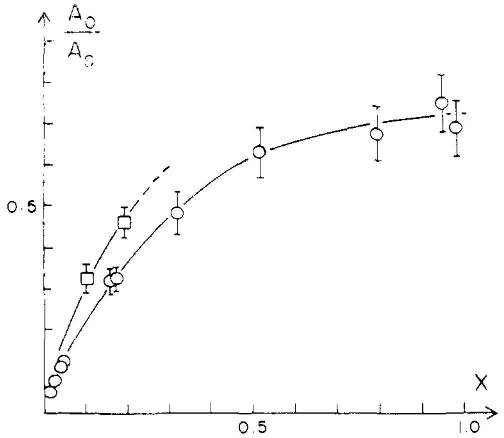

Fig. 4.—Plot of the total relative yield of labeled products as function of the mole fraction of methane; scavenger present; moderators: helium ○, neon □.

Formation of hot products at the surface of the reaction vessel cannot be considered important, since changes in the surface to volume ratio did not affect the yields of methane or methyl halide. Another argument is the calculation made on the diffusing, thermalized tritium atoms (Table III and appendix II). In pure methane only about 10% of these atoms would reach the walls, a fraction not nearly large enough to account for the yields observed. Furthermore, a mechanism involving diffusion would make the yields temperature and pressure dependent, in contrast to the observations.

Some radiation induced exchanges leading to production of labeled compounds probably will occur in the system. However, with data from investigations of the self-induced tritium labeling of methane,[8] it can be estimated that under the experimental conditions less than 1% of the actual amounts found can be formed in this manner. This is well within the experimental error.

The postulate of high-yield hot reaction between methane and tritium atoms is, however, in accord with all the data presented here. In particular, the noble gases do not act merely by diluting the methane (Fig. 1, 2, 3). Samples with the same mole fraction of one of these gases gave different yields, the yields decreasing in the order Xe, Ar, Ne, He. This is the expected behavior if the idea of hot reactions is adopted, since the efficiency of these gases in moderating the recoiling tritium atoms increases through this series. Furthermore, as is shown in the accompanying paper[6] a kinetic reaction model applicable only to hot reactions provides a satisfactory quantitative description of this system.

The mechanism of this hot hydrogen atom reaction appears to involve a fast displacement process.[2,3] An intermediate metastable complex of the type CH_4T in which all the hydrogens are equivalent appears most unlikely. By purely statistical consideration such a complex should give a yield ratio of HT to $CH_3T\cdot$ of 2/3. Even making allowance for a possible isotope effect this is completely incompatible with the observed ratio of 9/1. The detailed mechanism of the fast displacement is being investigated in other systems.

Appendix I

Recoil Loss.—Immediately after formation a fraction of the tritons will recoil into the walls with no possibility for reacting with molecules in the gas. This recoil loss can be calculated from purely geometrical considerations.

An ampoule has the shape of a cylinder, with radius R. If a triton is formed at a point 0 and if its recoil range is r, it may at the end of its track be at any point on the surface of sphere with center at 0 and radius r. The probability that the triton will hit the cylinder wall is then equal to that fraction of the spherical surface which is outside the cylinder. This fraction must then be averaged over all positions of 0 inside the cylinder.

For a cylinder of infinite length the recoil loss, L, is found to be

$$r < 2R\colon\ L = \frac{4}{3\pi}\left[\frac{C^2 - 1}{C}\,K(C) + \frac{C^2 + 1}{C}\,E(C)\right]$$

$$r > 2R\colon\ L = \frac{4}{3\pi}\left[(C^2 + 1)\,E\left(\frac{1}{C}\right) - (C^2 - 1)\,K\left(\frac{1}{C}\right)\right]$$

where $C = r/2R$, and K and E the complete elliptic integrals of the first and second kind respectively.

These expressions need only small corrections to apply to cylinders of finite length if $h/r \gtrsim 10$, h being the length of the cylinder.

In calculation of the recoil range, r, the following values employed for 0.192 mev. tritons (in gases at 76 cm., 0°)[10,11] were CH_4, 0.24; He, 1.45; Ar, 0.275; Ne, 0.82, and Xe, 0.17 cm.

Appendix II

Diffusion Loss.—The formulas given in appendix I can be used to find the diffusion loss, when an estimate has been made of the "diffusion range."

A treatment of random diffusion combined with simple gas-kinetic theory, leads to the expression[12]: $\Delta^2 \backsimeq \nu\lambda t$ where Δ^2 is the mean square displacement of a particle from the origin, ν the average velocity, λ the mean free path and t the time taken for the displacement. (Considering the uncertainty in these parameters, there is little point in using formulas more refined than the above.) Neglecting other thermal reactions, t will be determined by the rate of the reaction

$$T + CH_4 \longrightarrow HT + CH_3{}^{13,14}$$

---

(10) C. J. Cook, E. Jones and T. Jørgensen, *Phys. Rev.*, **91**, 1417 (1953).

(11) W. Whaling, "Handbuch der Physik," Vol. XXXIV, 1958, p. 208.

(12) E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd Ed., London, 1957, p. 67.

(13) M. R. Berlie and D. J. LeRoy, *Can. J. Chem.*, **32**, 650 (1954).

(14) R. Klein, J. R. McNesby, M. D. Scheer and L. J. Schoen, *J. Chem. Phys.*, **30**, 58 (1959).

ν and λ were calculated from the standard gas-kinetic expressions.

The loss found in this way must be multiplied by the probability of a tritium atom reaching thermal energies. This probability is approximately equal to $1 - A_0/A_s$, values of which can be found from Fig. 4.

Acknowledgments.—The authors wish to thank Professor L. Onsager for stimulating discussions of the mechanisms of hot reaction and for help with the calculations of the recoil loss. Suggestions of Professor F. S. Rowland regarding recoil ranges are gratefully acknowledged. Comparisons with the work of T. Pratt on radiation induced exchange reactions was very useful. Mr. Pratt also provided much help on problems of technique. This work was performed under the auspices of the United States Atomic Energy Commission.

[CONTRIBUTION NO. 1565, STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, NEW HAVEN, CONNECTICUT]

Kinetic Theory of Hot Atom Reactions: Application to the System H + CH_4

BY PEDER J. ESTRUP[1] AND RICHARD WOLFGANG

RECEIVED JULY 23, 1959

A model has been developed for the kinetics of hot atom reactions in the gas phase. An expression is derived giving the total probability that a hot atom will react before losing its excess energy, in terms of the average collisional energy loss and the efficiency of reaction upon collision. The model predicts the relative effect of inert moderating compounds and provides a measure of the relative energy at which various products are formed in reactions with a given substance. The theory is tested using experimental data on the action of moderators on the reactions of hot hydrogen with methane and is found to provide a good representation of this system.

Introduction

Atoms having much higher kinetic energy than provided by the thermal motion of their surroundings are usually termed "hot" atoms. If such atoms take part in reactions before they have lost their excess energy, the processes are called "hot" reactions.

In recent years several systems have been found in which hot atoms, produced by photochemical or nuclear processes, could be unambiguously shown to undergo hot reactions.[2–5] These hot reactions were identified by one or more of several characteristic features which serve to distinguish them from thermal reactions:

(1) Since the energy required for the reaction is almost exclusively supplied by the hot atom rather than by the environment, the hot reactions are to a first approximation temperature independent.

(2) The hot species rapidly loses its excess energy to the surroundings. Thus, any reaction must take place in one of the relatively few collisions that it makes before it is thermalized. Hot reaction yields are therefore independent of minor constituents, in particular scavengers (such as I_2) which may be added to remove reactive thermal species.

(3) Hot reactions are sensitive to moderators (*e.g.*, helium) which, though chemically inert, will efficiently remove energy from the hot species.

The detailed experimental investigation of the effect of moderators on the hot reactions of hydrogen atoms with methane[5] has provided a stimulus for attempting to develop a quantitative model of hot atom kinetics. Evidently models involving an equilibrium distribution of thermal energies, such as that leading to the Arrhenius equation $k = pZe^{-\Delta E/RT}$ and its variants[6] will not be applicable to hot species since, by definition, these are outside such an equilibrium distribution. Furthermore, hot species may in general be expected to react well above the "activation energy" ΔE, and it seems quite likely that p, the "steric factor" cannot be considered constant when the available energy exceeds ΔE. Indeed the variation of p with energy is a central problem in high-energy kinetics.

Using a rather simple model of hot atom reactions this study attempts to describe their kinetics and develops an equation which might be considered a hot atom analog of conventional rate expressions for thermal systems.

Model

Consider a system which is comprised of hot atoms of initial energy E_0, in a thermal environment consisting of one or more components. The hot atoms lose energy in successive collisions but may react to enter combinations over a certain energy range E_2 to E_1. Above E_2 the collisions are too energetic to result in stable combinations, while E_1 is the minimum energy required for reaction.

The reaction probability per collision between the hot atom and a molecule of component j is denoted by $p_j(E)$ where this quantity is finite in the interval $E_2 > E > E_1$ and zero elsewhere. ($p_j(E)$ corresponds to the collision efficiency $pe^{-\Delta E/RT}$ in normal kinetic terminology. However, since for hot atoms $E > \Delta E$ and $e^{-\Delta E/RT} \sim 1$, $p_j(E)$ becomes a high energy equivalent to the "steric factor," p.) Then if N_s is the total number of hot atoms available for reaction and if f_j is the relative probability of collision with compound j, the number of hot combination products is

$$N_{\text{hot}} = N_s \sum_j \int_{E_2}^{E_1} f_j p_j(E) n(E)\, dE \qquad (1)$$

where $n(E)dE$ is the number of collisions suffered between $E + dE$ and E.

---

(1) CERN, Geneva, Switzerland. Work performed in partial fulfilment of the requirements for the Ph.D. degree at Yale University.

(2) H. A. Schwarz, R. R. Williams and W. H. Hamill, THIS JOURNAL, **74**, 6007 (1952).

(3) R. J. Carter, W. H. Hamill and R. R. Williams, *ibid.*, **77**, 6457 (1955).

(4) M. Amr El-Sayed, P. J. Estrup and R. Wolfgang, *J. Phys. Chem.*, **62**, 1356 (1958).

(5) P. J. Estrup and R. Wolfgang, THIS JOURNAL, **82**, 2661 (1960).

(6) A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press, Inc., New York, N. Y., 1955.