J. Chem. Soc., Faraday Trans. 1, 1981, 77, 187–195

Recoil Tritium Reactions with Molecular Hydrogen

Part 1.—Scavenger Effects

By David J. Malcolme-Lawes,* Graham Oldham
and Yacoub Ziadeh

Chemistry Department, Loughborough University of Technology, Leicestershire

Received 10*th January*, 1980

Scavenger curves for O_2, Br_2 and ICl scavengers have been obtained in the $T+H_2$ system moderated by helium, argon and krypton. Results indicate that scavenger competition is significant with all three scavengers but that the behaviour of oxygen scavenger is also sensitive to the nature of the moderator present. It is suggested that this behaviour arises because of the three-body nature of the oxygen scavenging process.

The hydrogen atom exchange reaction

$$H+H_2 \rightarrow H_2+H \tag{1}$$

is generally regarded as the prototype reaction of chemistry at ordinary energies and, together with its isotopic analogues, has formed the subject of many experimental and theoretical studies. It would seem reasonable to suppose that these same reactions at high collision energies would form the prototype systems of hot-atom chemistry.[1] However, of the many papers on hot-atom chemistry during the last two decades,[2] very few have been concerned specifically with the hot hydrogen isotopic exchange reaction. In spite of this these fundamental reactions are of considerable interest because they are amenable to detailed theoretical calculations [indeed the most accurately known potential energy surface for a polyatomic system is that for reaction (1)] and some of them may be studied by relatively well developed hot-atom techniques. These factors should should allow valuable comparisons to be made between theory and experiment.

While there have been many theoretical calculations[3-9] of the potential energy surface for the H_3 system involved in reaction (1), only a small number of papers has appeared relating such surfaces to reaction probabilities or cross-sections. Excitation functions have been predicted[7, 10-12] for reactions (2)-(5) and the corresponding three-atom dissociation processes,

$$T+H_2 \rightarrow HT+H \tag{2}$$

$$T+D_2 \rightarrow HT+D \tag{3}$$

$$T+HD \rightarrow HT+D \tag{4}$$

$$\rightarrow DT+H. \tag{5}$$

However, relating the calculated excitation functions to experimental measurements has been unfruitful, largely because of the paucity of experimental data. With one early exception,[13] the experimental data on reactions (2)-(5) rests essentially on two communications by Wolfgang and coworkers[14, 15] which appeared before some of the experimental problems now associated with the recoil tritium technique became apparent, and one by Hawke and Moir.[16] Other experimental papers[17] have dealt with reactions (2) and (3), but as reactions in competition with more complex processes and so not directly relevant to what follows. Similarly studies using photogenic tritium atoms[18] have been reported although, of course, such atoms are confined to the low-energy end of the hot-reaction region.

We have undertaken a detailed study of reactions (2)-(5) using the nuclear recoil technique with the aim of comparing experimental product yields with values predicted from classical trajectory calculations.[7] In this paper we report experiments performed on the $T+H_2$ system with the more limited objective of characterising a scavenger species for subsequent use in moderation studies.

EXPERIMENTAL

METHODS

The experimental techniques for studying the reactions of tritium atoms recoiling from the $^3He(n, p)^3H$ process are well established and have been adequately detailed elsewhere.[1] In principle a sample bulb is filled with the reactant material, a thermal atom and radical scavenger, a small amount of helium-3 and, in some cases, an inert moderator. The sample bulb is sealed and irradiated with a thermal neutron flux to induce an activity of *ca.* 40 kBq of tritium. The contents of the bulb are then analysed by radio-gas-chromatography, the activities of the reaction products measured and coverted into fractional yields (P_i for product i) after dividing the product activity by the total activity of tritium stopped in the gas phase. (Some of the tritium formed recoils into the wall of the sample bulb and is not available for reaction in the gas phase.)[19]

The $T+H_2$ system should be relatively straightforward when studied by the technique outlined above because (*a*) the only reactions which lead to tritiated products are (2) and the thermal scavenging reaction and (*b*) reaction (2) is known to have an appreciable activation energy[20] (*ca.* 30 kJ mol^{-1}) so that thermal reaction should be negligible at room temperature if a highly reactive scavenger is present. Unfortunately both factors give rise to difficulties and could produce massive errors in the P_{HT} yields from reaction (2).

The fact that only one hot-reaction product is obtained from the $T+H_2$ system results in only a single product activity being measured. (It is not generally a practical proposition to measure scavenged tritium activity with a high degree of accuracy owing to the ease with which isotopic exchange may occur.) Consequently the product yield must be obtained using an indirect estimate of the tritium activity stopped in the gas phase. (In other recoil tritium systems, such as $T+C_2H_6$, several different products are generally formed and activity ratios may be used in evaluating results.) It has long been recognised that the activity of tritium stopped in the gas phase, A_T, can be calculated using[19]

$$A_T = A_I(I-L) \tag{6}$$

where A_I is the activity induced in the sample bulb and L is the recoil loss fraction, *i.e.* the fraction of tritium formed which recoils into the wall of the sample bulb.

L can be calculated[19, 21, 22] for a sample bulb of given dimensions if the range of the 0.192 MeV tritons formed by the nuclear reaction in the sample gas is known. Unfortunately ranges of 0.192 MeV tritons in gases have not been measured experimentally and these recoil ranges have generally been inferred from proton stopping powers. Recent calculations have indicated that recoil tritium ranges in many gases may have been overestimated in the past,[23] and quite seriously so for the low mass gases H_2 and He. Such overestimates result in an overestimate of L, an underestimate of A_T and consequently calculated fractional yields of hot products which are too large.

The recoil ranges used for calculating L in this work are collected in table 1.[24]

The second factor which may lead to errors in P_i determination is 'scavenger competition'.[25] Scavengers such as bromine may compete with the prime reactant for tritium atoms in the hot-energy region of recoil tritium/hydrocarbons systems.[1] Other scavengers, particularly

TABLE 1.—192 keV TRITON RECOIL RANGES USED IN ESTIMATING RECOIL LOSS

gas	range at s.t.p./cm
H_2	0.426
He	0.937
Ar	0.480
Kr	0.393
O_2	0.217
Br_2	0.101
ICl	0.090

molecular oxygen, may scavenge tritium atoms to form radical species (*e.g.* TO_2) whose subsequent reactions are not fully understood. Either or both of these complications may give rise to an experimentally measured product yield which does not reflect simply the hot reactivity of the prime reactant (*i.e.* H_2 in our system). The nature of these possible scavenger interferences is such that their absence should be assured[25-27] if the hot-product yield is demonstrated to be independent of the scavenger concentration over the concentration range of interest (typically 1-5 mol %). We have examined three possible scavengers for use in the $T + H_2$ system: molecular oxygen, bromine and iodine monochloride. The results obtained with these scavengers are considered below.

MATERIALS

Sample bulbs, *ca.* 60 × 18 mm, were fabricated from Vitreosil tubing (Jencons), and filled on a grease-free vacuum line with the reagent gases: oxygen (purity 99.5%), helium-4 (purity 99.80%), argon (purity 99.8%), supplied by B.O.C., krypton (purity $>$ 99.995%), Air Products, bromine (purity $>$ 99.0%), Fisons Scientific Apparatus, and iodine monochloride (purity $>$ 98%), Hopkin and Williams. Helium-3 was supplied by the Radiochemical Centre, with a stated purity of $>$ 99.89% and a tritium level of $< 2 \times 10^{-10}$ mol %. The helium-3 was stored in a Pyrex bulb which had a nickel film deposited on the inside surface, to minimise T_2 contamination of the samples before irradiation.

Neutron irradiation was performed on the Herald reactor at Aldermaston so that samples received a total thermal neutron dose of *ca.* 10^{15} neutrons $cm.^{-2}$

Analysis of the samples was performed by radio-gas-chromatography using a 2 m alumina column with katharometer and twin gas-flow proportional counters.[28] The chromatographic carrier gas was helium and this was mixed with *ca.* 10 vol. % methane before entry to the proportional counters.

RESULTS AND DISCUSSION

Yields of HT as a fraction of the tritium activity stopped in the gas phase and as a function of the mol % of scavenger were determined in excess of each of three inert moderators: helium, argon or krypton. The results are shown as scavenger curves in fig. 1-3, for O_2, Br_2 and ICl scavenger, respectively. In each figure the solid lines indicate the linear portion of each scavenger curve, while the broken lines indicate the departure from linearity consistent with inadequate scavenging.[25, 26] In the absence of scavenger all samples contained *ca.* 6 mol % H_2, 90% moderator and 4% helium-3, and the total pressure was equivalent to *ca.* 100 cmHg. The superimposition of the results from krypton and argon moderated systems in fig. 2 and 3 is coincidental.

Qualitatively each of the scavenger curves appears normal,[26] showing a linear portion exhibiting a slight negative slope and a rapid rise towards $P_{HT} = 1$ at low scavenger concentrations where scavenging is inadequate and HT is produced by

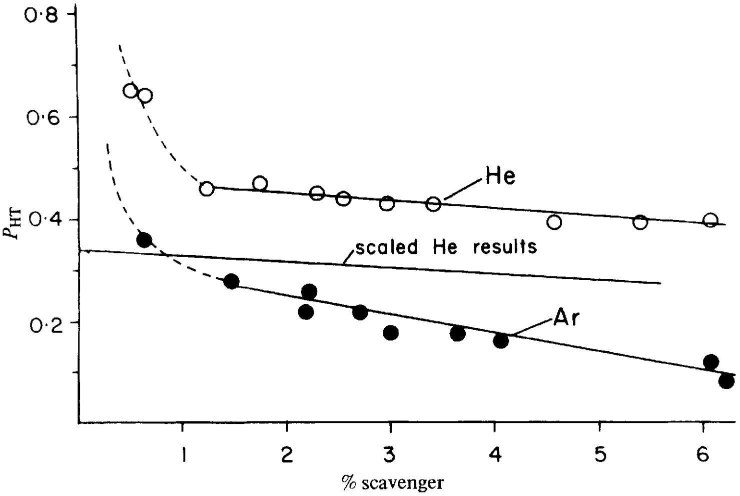

FIG. 1.—Experimental scavenger curves for oxygen scavenged H_2 in the presence of helium and argon moderators. Also shown is the line corresponding to the helium moderated scavenger curve scaled to pass through the intercept of the argon curve.

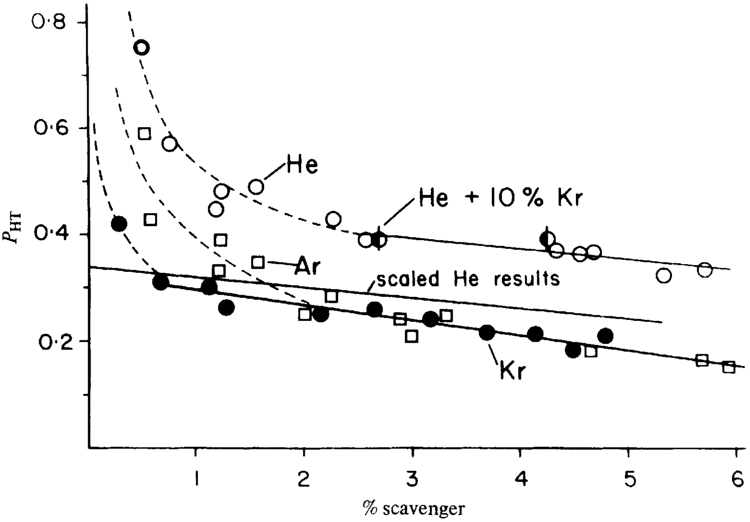

FIG. 2.—Experimental scavenger curves for H_2 scavenged by bromine and moderated by helium, argon and krypton.

thermal reactions. The scavenger-corrected kinetic theory[26] of hot-atom reactions predicts that the hot-product yield, P_i, is given by

$$P_i = \left(\frac{f_r}{\alpha}\right) I_i - \left(\frac{f_r}{\alpha}\right)^2 \left(K_i + \frac{f_s}{f_r} K_i'\right) \qquad (7)$$

where α is mean logarithmic energy decrement for collisions involving hot atoms,[1, 2] given by

$$\alpha \equiv \Sigma_c f_c \alpha_c$$

where f_c is the probability of collision of hot atom with component c, and α_c is defined as $\langle \ln (E/E') \rangle$ averaged over collisions between hot atoms (at initial energy E)

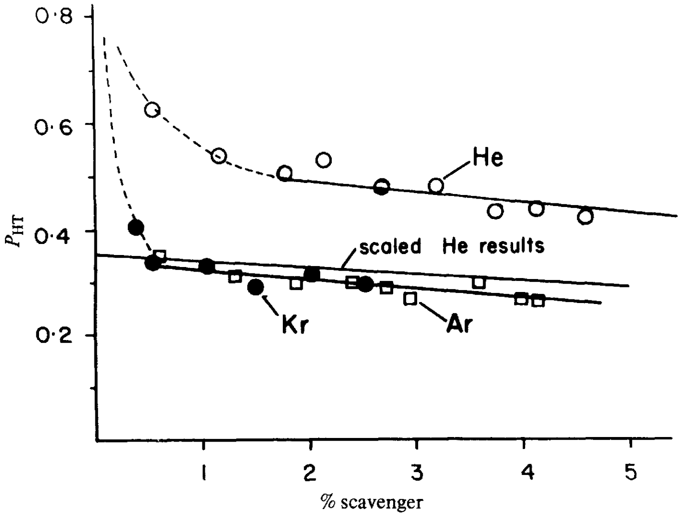

FIG. 3.—Experimental scavenger curves for H_2 scavenged by iodine monochloride and moderated by helium, argon and krypton.

and molecules of component c, to produce hot atom energy E'. I_i is the reactivity integral for formation of product i, given by

$$I_i \equiv \int_0^\infty \frac{p_i(E)}{E} \mathrm{d}E,$$

with $p_i(E)$ the probability of reaction on collision between hot atom and reactant at collision energy E.

$$K_i = \int_0^\infty \frac{p_i(E)}{E} \int_E^\infty \frac{\sum_j p_j(E'')}{E''} \mathrm{d}E'' \, \mathrm{d}E$$

and

$$K_i' = \int_0^\infty \frac{p_i(E)}{E} \int_E^\infty \frac{p_s(E'')}{E''} \mathrm{d}E'' \, \mathrm{d}E$$

with $p_s(E)$ the probability of reaction on collison between hot atom and scavenger at collision energy E.

When scavenger curves are plotted using f_s as the abscissa, then, for a range of f_s over which $\mathrm{d}\alpha/\mathrm{d}f_s$ may be neglected,

$$\frac{\mathrm{d}P_i}{\mathrm{d}f_s} \equiv -\frac{f_r K_i'}{\alpha^2} \qquad (8)$$

gives a measure of the extent of scavenger competition for hot atoms. Extrapolation of this linear portion of the scavenger curve to $f_s = 0$ yields the intercept

$$P_i^0 = \left(\frac{f_r}{\alpha}\right) I_i - \left(\frac{f_r}{\alpha}\right)^2 K_i \qquad (9)$$

where P_i^0 represents the hot yield which would be observed in the absence of scavenger competition, *i.e.* if $p_s(E) = 0$ for $E >$ threshold for reaction between hot atoms and reactant species.

In the absence of a reliable method for estimating f_c values in the hot or epithermal energy ranges, scavenger curves are usually plotted as a function of scavenger mole fraction, x_s (or mol % as in fig. 1-3). In this case

$$\frac{dP_i}{dx_s} = -A\frac{f_r}{\alpha^2}K_i' \tag{10}$$

represents the slope of the scavenger curve and A is a constant of the system, provided that x_s is sufficiently small for the relation between x_s and f_s to be taken as linear. Extrapolation of this slope back to $x_s = 0$ will, of course, lead to the same result as eqn (9).

As the extrapolated hot yield is predicted to be independent of the nature of the scavenging species, the P^0_{HT} values determined from the curves in fig. 1-3 should be dependent only on (f_r/α) and so, in our systems, only on the moderator used. The P^0_{HT} values derived from fig. 1-3 are shown in table 2, and clearly the agreement between the values obtained from the different scavengers is excellent, indicating a 'true' hot yield of *ca.* 0.34 in the argon or krypton moderated systems and *ca.* 0.48 in helium.

TABLE 2.—HT YIELDS IN DIFFERENT MODERATORS AND SCAVENGERS EXTRAPOLATED TO ZERO SCAVENGER CONCENTRATION

	extrapolated HT yield, P^0_{HT}	
scavenger	in helium	in argon/krypton
O_2	0.48 (±0.05)	0.34 (±0.03)
Br_2	0.47	0.34
ICl	0.52	0.34

Eqn (7) and (9) may be combined to give

$$P_i = P_i^0 - \left(\frac{f_r}{\alpha}\right)\left(\frac{f_s}{\alpha}\right)K_i' \tag{11}$$

and the yields obtained in different moderators may be compared by scaling the yields so that, for a given scavenger, the scavenger curves in the different moderators have the same intercept and so effectively the same (f_r/α) value. As the argon and krypton curves we obtained (in Br_2 and ICl) were essentially identical over the linear ranges, we have chosen to scale the yields obtained in helium moderator by

$$\frac{P^0_{HT}(\text{Ar})}{P^0_{HT}(\text{He})} = \frac{0.34}{0.48} = 0.72.$$

The results are shown by the lines marked as 'scaled He results' in fig. 1-3. These curves represent the effects of the various scavengers at an approximately constant value of (f_r/α) in argon and helium moderators. In each case there is significantly more scavenger competition in the argon-moderated systems than in those moderated by helium. That this is to be expected may be seen from eqn (10), where K_i' is independent of moderator but α_m for argon is considerably smaller than for helium.

Both curves for bromine scavenger (fig. 2) show greater (negative) slopes than their counterparts for ICl scavenger, indicating that scavenger competition is more significant in the Br_2 scavenged systems than in ICl, so that AK'_{HT} is greater for Br_2

than for ICl. The curves for oxygen scavenger appear to be anomalous, in that there is a greater change of slope in going from helium moderator to argon moderator than is the case for either of the other scavengers. The slopes of all curves in fig. 1-3 are collected in table 3.

The anomalous behaviour in oxygen scavenger is more clearly demonstrated by comparing the three scavenger curves obtained in helium moderator with the three obtained in argon moderator, as shown in fig. 4. In helium moderator the extent of oxygen scavenger competition (*i.e.* the slope of the scavenger curve) is intermediate between the scavenger competition of Br_2 and ICl. However, in argon moderator oxygen exhibits more scavenger competition than either of the other scavengers. Clearly the anomaly would persist if the scavenger curves were plotted as functions of f_S (rather than x_S), for any reasonable values of the total cross-sections, so that one is forced to conclude that for oxygen scavenger K'_{HT} must be greater in the presence of excess argon than in the presence of excess helium. The definition of K'_i [see eqn (7)] requires in turn that the cross-section for the oxygen scavenger competition process is dependent on the nature of the 'inert' moderator.

TABLE 3.—SLOPES[a] OF NORMALISED SCAVENGER CURVES

scavenger	moderator helium	argon
O_2	1.7	4.3
Br_2	2.8	3.3
ICl	2.0	2.3

[a] dP_{HT}/dX_S, error limits ±20%.

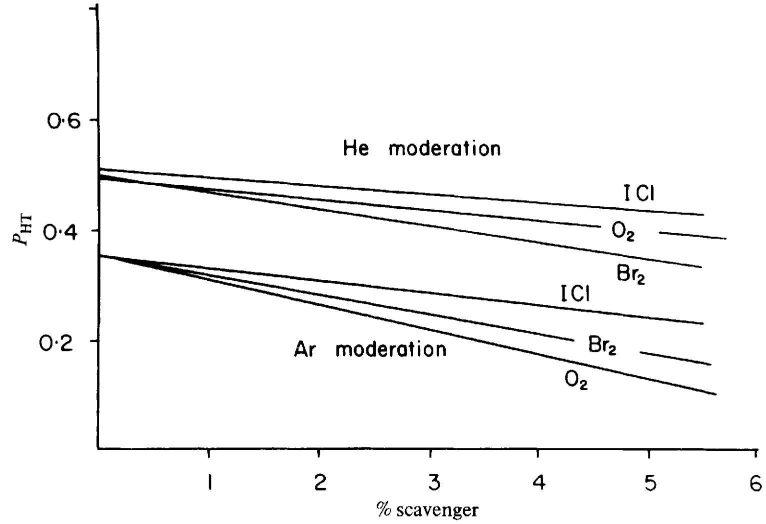

FIG. 4.—Extrapolated scavenger curves for H_2 moderated by helium and argon, showing the different order of scavenger competition effect in the two moderators.

While the scavenger competition process in Br_2 (and indeed the basic scavenger reaction) is assumed to be reaction (12),[29]

$$T + Br_2 \rightarrow TBr + Br^{\cdot} \tag{12}$$

the mechanism of oxygen scavenger competition is not fully understood. While reaction (13) is likely to be important at high energies, reaction (14) is undoubtedly the dominant process at thermal energies

$$T + O_2 \rightarrow TO + O \tag{13}$$

$$T + O_2 + M \rightarrow TO_2 + M. \tag{14}$$

In thermal systems the H-atom analogue of reaction (14) has been extensively studied and is thought to occur by both energy-transfer and complex-formation mechanisms,[30] reactions (15) and (16), respectively

$$H + O_2 \rightarrow HO_2{}^* \tag{15a}$$

$$HO_2{}^* + M \rightarrow HO_2 + M \tag{15b}$$

$$O_2 + M + M \rightarrow O_2M + M \tag{16a}$$

$$H + O_2M \rightarrow HO_2 + M. \tag{16a}$$

As the cross-section for reaction (13) is not expected to be sensitive to the nature of any moderating species present, we must consider the likely effects of helium and argon moderators as the third bodies for reaction (14) in the epithermal and hot regions where scavenger competition effects are likely to occur. Considering first mechanism (15), in which a vibrationally excited radical is formed, it is unlikely that such radicals in the present hot tritium system will be formed with high translational energies because of the difference in mass between the reacting species. Thus the relative efficiency of the energy transfer process (15*b*) is likely to be similar to the relative efficiency of similar processes at thermal energies. Ahumada *et al.*[31] have estimated the relative deactivation efficiency ratios of HCO*, HNO* and HO_2^* by argon and helium third bodies to be 1.3, 1.2 and 1.1, respectively, although the uncertainties in these values (which were based on collision rates calculated using averaged Lennard-Jones diameters for the radicals) must remain rather high. As expected these estimates indicate that the probability of stabilisation of the excited radical by collision increases as the mass of the third body increases, and we anticipate that argon will be a more effective third body than helium in a scavenger competition process proceeding *via* the energy transfer mechanism (15).

The complex formation mechanism (16)[32] requires that bound states occur in Lennard-Jones complexes. It is unlikely that such states would arise with low-mass third bodies, so that the complex mechanism should not be important in the helium-moderated hot tritium system. For higher-mass third bodies it has been argued that in both $H + O_2 + M$ and $H + NO + M$ thermal systems, a partial contribution *via* complex formation to the overall reaction rate exists,[31] an argument similar to that put forward in the case of the iodine atom recombination reaction $I + I + M$.[33] Thus any contribution to the scavenger competition process in the present hot tritium system occurring *via* complex formation is likely to enhance scavenger competition in the argon moderated system compared with the helium moderated system.

It would seem that the anomalous behaviour of oxygen as a scavenger in the $T + H_2$ system derives from the three body nature of the scavenging reaction (14). The implications of this factor extend beyond the $T + H_2$ system to the considerable amount of work reported on recoil tritium/hydrocarbon systems.[1, 2] There are two main reasons why the oxygen anomaly will require examination in hydrocarbon systems: (1) hydrocarbons have lower reactivities than H_2 (*i.e.* yields are lower) and the effects of scavenger competition are likely to be more important for systems in which more tritium atoms reach the lower energy region of the hot reaction zone; (2) hydrocarbon molecules being polyatomic species are likely to make excellent third bodies for reaction (14) compared with the inert-gas moderators.

CONCLUSION

Our results suggest that scavenger competition is significant in the $T+H_2$ system when Br_2, ICl or oxygen are used as scavengers. The extent of this scavenger competition is smallest in the case of ICl scavenger, and for both ICl and Br_2 scavengers can be handled using the scavenger corrected kinetic theory. For oxygen scavenger, the extent of scavenger competition varies with the nature of the moderating species in a manner which cannot be simply quantified using the existing corrections to the kinetic theory. It is likely that this oxygen anomaly arises because of the three-body nature of the scavenging reaction.

As ICl shows the least influence on hot product yields we conclude that ICl is the most appropriate scavenger for use in studies of the recoil $T+H_2$ systems.

This work was supported by the S.R.C. The authors thank the staff of the A.W.R.E. Herald reactor for irradiating the samples.

[1] D. S. Urch, *Radiochem.*, 1975, **2**, 1.
[2] D. S. Urch, *Int. Rev. Sci.*, Ser 2, *Radiochemistry*, ed. A. G. Maddock, (1975), vol. 8, p. 49.
[3] R. N. Porter and M. Karplus, *J. Chem. Phys.*, 1964, **40**, 1105.
[4] J. K. Cashion and D. R. Herschbach, *J. Chem. Phys.*, 1964, **40**, 2358.
[5] I. Shavitt, R. M. Stevens, F. L. Minn and M. Karplus, *J. Chem. Phys.*, 1968, **48**, 2700.
[6] H. Conroy and B. L. Bruner, *J. Chem. Phys.*, 1967, **47**, 921.
[7] D. J. Malcolme-Lawes, *J. Chem. Soc., Faraday Trans. 2*, 1975, **71**, 1183.
[8] J. M. Norbeck and P. R. Certain, *J. Chem. Phys.*, 1975, **63**, 4127.
[9] P. Siegbahn and B. Liu, *J. Chem. Phys.*, 1978, **68**, 2457.
[10] M. Karplus, R. N. Porter and R. D. Sharma, *J. Chem. Phys.*, 1966, **45**, 3871.
[11] J. T. Adams and R. N. Porter, *J. Chem. Phys.*, 1973, **59**, 4105.
[12] J. S. Wright, S. K. Gray and R. N. Porter, *J. Phys. Chem.*, 1979, **83**, 1033.
[13] J. K. Lee, B. Musgrave and F. S. Rowland, *J. Chem. Phys.*, 1960, **32**, 1266.
[14] D. Seewald, M. Gersh and R. Wolfgang. *J. Chem. Phys.*, 1966, **45**, 3870.
[15] D. Seewald and R. Wolfgang, *J. Chem. Phys.*, 1967, **46**, 1207.
[16] J. G. Hawke and J. Moir, *J. Chem. Soc., Chem. Commun.*, 1974, 490.
[17] J. W. Root and F. S. Rowland, *J. Chem. Phys.*, 1967, **46**, 4299; *J. Phys. Chem.*, 1970, **74**, 451.
[18] C. C. Chou and F. S. Rowland, *J. Chem. Phys.*, 1967, **46**, 812.
[19] P. J. Estrup, *Ph.D. Thesis* (Yale University, 1959).
[20] A. Kuppermann and J. M. White, *J. Chem. Phys.*, 1966, **44**, 4352.
[21] W. J. Arbersinger, *J. Phys. Chem.* 1963, **67**, 976.
[22] J. Root and F. S. Rowland, *Radiochim. Acta*, 1968, **10**, 104.
[23] D. J. Malcolme-Lawes, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 860.
[24] C. S. Zaidins, *Nuclear Instrum. Methods*, 1974, **120**, 125.
[25] D. J. Malcolme-Lawes, *Radiochim. Acta*, 1971, **16**, 57.
[26] D. J. Malcolme-Lawes, *J. Chem. Phys.*, 1972, **57**, 2476.
[27] D. J. Malcolme-Lawes, *J. Chem. Phys.*, 1972, **57**, 2481.
[28] D. J. Malcolme-Lawes, *Radiochem. Radioanal. Lett.*, 1971, **6**, 31; 1971, **7**, 101.
[29] D. J. Malcolme-Lawes, *J. Chem. Soc., Faraday Trans. 2*, 1978, **74**, 182.
[30] D. L. Bunker, *Theory of Elementary Gas Reaction Rates* (Pergamon, London, 1966), p. 76.
[31] J. J. Ahumada, J. V. Michael and D. T. Osborne, *J. Chem. Phys.*, 1972, **57**, 3736.
[32] D. L. Bunker and N. Davidson, *J. Am. Chem. Soc.*, 1958, **80**, 5090.
[33] H. S. Johnston, *Gas Phase Reaction Rate Theory* (Ronald, New York, 1966), p. 253.

(PAPER 0/054)