GAS PHASE HYDROGEN ATOM RECOMBINATION

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Recombination rate measurements are presented for the reaction $H+H+M\rightarrow H_2+M$ for $M=N_2$, CH_4, CO_2, and SF_6 at temperatures from 77 to 295°K for N_2 and CH_4, and about 160 to 295°K for CO_2 and SF_6. Data from our earlier work on $M=H_2$, He and Ar are included, all rate constants are tabulated and their ratios and temperature dependences are discussed. Compared to $k^{H_2}=8.1\times10^{-33}$ cm^6 sec^{-1} (specific rate constant, $T=295°K$) k^M/k^{H_2} ratios are 0.87, 1.14, 1.13, 1.89, 2.02, and 2.41 in the order $M=$He, Ar, N_2, CH_4, CO_2, SF_6. Temperature dependences of k^M, in T^{-n} form are $n=0.60$ for H_2 and 0.40, 0.81, 1.33, 1.2, 2.27, and 1.8 for the other M in the above order. Comparison with theoretical calculations suggests that the recombination proceeds almost entirely by the energy transfer mechanism and that quantum-mechanical resonances are important intermediates at low temperatures. The results are compared with other published data and attempts are made to correlate them with high temperature results from flame and shock tube studies.

Introduction

Premixed flames are known to consist of a region in which exothermic reactions are initiated by radical diffusion and heat conduction and rapidly proceed to a state of partial equilibrium, followed by a larger region in which relatively slow recombination reactions remove excess concentrations of atoms and radicals, give rise to a further temperature increase, and take the gas to thermodynamic equilibrium. For fuel-rich H_2/O_2 flames, for example, these recombination steps are mainly $H+H+M\rightarrow H_2+M$ and $H+OH+M\rightarrow H_2O+M$. Order of magnitude calculations show that at 1500°K the principal bimolecular reactions of H and OH have rate constants in the 10^{-12} to 10^{-11} cm^3 molecule^{-1} sec^{-1} range, whereas the equivalent second-order rate constant for H-atom recombination at 1 atm pressure is about 100 times smaller, and the disparity between the rates of these processes is further increased by the fact that the reaction partners in some of the bimolecular radical-molecule reactions are present in large concentration. Clearly, then, information is required on the exact magnitude, temperature-, and M-gas-dependence of simple recombination rate constants in order to understand and model flame processes. Yet, a glance at the massive review by Baulch *et al.*,[1] of published work on

$H+H+M\rightarrow H_2+M$ up to 1971, which includes 207 references, demonstrates the severe lack of agreement among the results of different investigators in all three experimental temperature domains: from below to slightly above 300°K in flow tube studies; in the 1000 to 2000°K range in flame studies; and from 2000 to 7000°K in shock tube work, the latter deriving recombination data principally from dissociation rate measurements.

Similarly, many theoretical models of atom recombination processes have been developed, beginning with Bodenstein's[2] simple scaling of such processes by the ratio of molecular diameter to mean free path, Tolman's[3] interaction width, to modern theories which describe (a) the stepwise energy transfer (ET mechanism) by which stable molecules are formed from unbound collision pairs[4] and/or (b) the formation and subsequent reaction of weakly bound radical-molecule complexes (RMC mechanism) in those cases where the atom-M-gas interaction is sufficiently strong.[5] These theories, whether dynamical or statistical,[6,7] are necessarily complex, because they require detailed, generally unavailable information on various potential energy surfaces for greatly extended molecules or pseudo-molecules. Their range of predictions has been quite diverse, but, as the range in the absolute magnitude of recombination rate con-

stants is small and the temperature dependence weak, the poor reliability of the older experimental data has made a critical comparison impossible.

The present experimental work on H-atom recombination was begun originally to assess the importance of quantum effects, i.e., of long-lived orbiting resonances[8,9] in the recombination process at low temperatures (77 to 298°K) for very simple M, viz He, Ar, and H_2.[10] Although this battle of the theorists on the merits of classical phase space versus resonance theories rages still, it does appear that the resonance theory is highly successful in fitting our published data.[9,10] This experimental work has now been extended to include M gases of greater interest in combustion processes such as N_2, CO_2, and CH_4, as well as SF_6 which is large and has low vibration frequencies. The temperature ranges covered are 77 to 295°K for N_2 and CH_4 and about 160 to 295°K for CO_2 and SF_6. Extension to higher temperatures is also being attempted but leads to formidable experimental problems due to increasingly rapid surface recombination.

Experimental

The apparatus is essentially that described in the earlier paper.[10] Briefly, it consists of a cylindrical flow tube, 100 cm long, 2.54 cm inside diameter, now modified to permit the addition of large flows of M-gases downstream of the H-atom source (a heated W-filament) but upstream of the temperature controlled section which is traversed by the isothermal catalytic probe detector which is one arm of a self-balancing dc Kelvin bridge. This detector (65 cm of 0.025 cm diameter of Pt/10%Rh wire), which has been shown to have unit efficiency in both H-atom removal and in energy accommodation, is entirely enclosed in the vacuum system and is controlled to move at any one of ten preselected steady speeds in the upstream direction into the flowing gas. A matched pair of such probe traversals, one with atom source on and another with atom source off, provide a continuous $[H]$ vs distance and thereby $[H]$ vs time plot. The latter transformation simply is $d/dt = \bar{v}d/dx$, i.e., one-dimensional plug flow applies under typical experimental conditions, e.g., $\bar{v} \sim 500$ cm sec^{-1}, $p \sim 6$ Torr, $[H] \lesssim 1\%$ of total pressure. The accuracy of the results is highly dependent on our success in keeping the simultaneous surface recombination of H-atoms as slow as possible. This is accomplished by coating the flow tube with metaphosphoric acid and by conditioning

in a stream of H-atoms over long periods (several days) which results in effective first-order surface recombination rate constants, k_w, in the range 0.1 to 0.2 sec^{-1} corresponding to recombination coefficients, γ, of 1 to 2×10^{-6} per collision, and assures that the surface contribution to the measured H-atom decay is less than 5%.

The following gases and purification procedures were used: H_2 (Matheson, ultra-high purity grade) was passed through a trap filled with molecular sieve (Baker, type 4A) at 77°K; N_2 (Matheson, O_2-free grade) was passed through a similar trap at 194°K; CH_4 (Matheson, ultra-high purity grade) was passed through a similar trap at 194°K; SF_6 (Matheson, C.P. grade) was frozen and pumped at 77°K and then passed through a similar trap at 225°K; CO_2 (Matheson, Coleman Instrument grade) was passed through a similar trap at 210°K. As an alternative source of CO_2 powdered dry ice was pumped at 77°K and then treated as above.

In all series of experiments, data were collected for pure H_2 and for 4 to 7 H_2-M mixtures at mole fractions X_M between 0.1 and 0.9. Cleanly linear $1/[H]$ vs distance plots provided second-order rate constants which were corrected for surface recombination and divided by total gas concentration to yield k^T. All k's are specific rate constants, i.e. $k \equiv d[H_2]/dt/[H]^2[M]$. On the assumption that this recombination rate constant, k^T, is a linear function of k^{H_2} and k^M, i.e. $k^T = k^M + (k^{H_2} - k^M)X_{H_2}$, plots of k^T vs. X_{H_2} will yield k^M on extrapolation to $X_{H_2} = 0$. This was usually a short extrapolation and in view of the linear behavior over the experimentally accessible range, as shown in a typical example for $M = CH_4$ in Fig. 1, is unlikely to lead to large errors. In all cases, the extrapolation was done with a least squares computer fit. The resulting ratio, k^M/k^{H_2}, was then combined with the best, averaged value for k^{H_2} at that temperature to give k^M. In the course of these experiments, it was gratifying to note the excellent constancy and reproducibility of k^{H_2} which thereby served as a secondary standard at all temperatures.

The major experimental difficulty in this work, apart from (a) continuous vigilance of maintaining a well-poisoned tube surface, and (b) equal vigilance of maintaining an unpoisoned, highly catalytic probe detector (which was occasionally reactivated by heating to dull red heat in an H_2-H flow) was the attainment of stable, flat temperature profiles at temperatures between 77 and 295°K and their perturbation by the heated, isothermal detector, as has been noted earlier.[10]
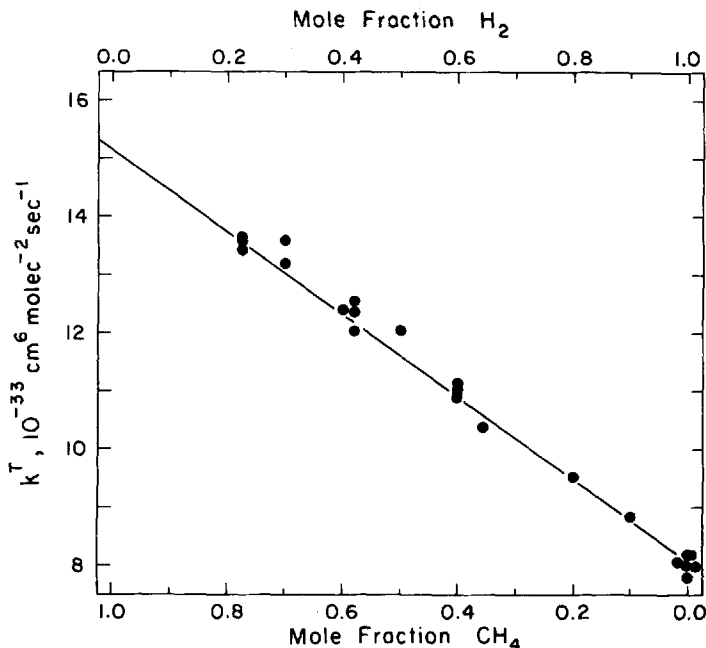
FIG. 1. Plot of Total Recombination Rate Constant k^T vs mole fraction of CH_4, X_{CH_4}, at 295°K.

Results

All experimental results of this study for $M =$ N_2, CH_4, CO_2, and SF_6 are presented in Table I and in Figs. 2 and 3, along with the earlier results[10] for $M = H_2$, He, and Ar. It should be noted that for N_2 and CH_4, k^M was measured at 77, ~180, and 295°K, for CO_2 at eight temperatures from 175 to 295°K, and for SF_6 only at 161 and 295°K. The stated uncertainties are the single standard deviations of the experimental results and do not include estimated systematic errors. These may range from about ±10% at 295°K to ±15% at much lower temperature, the latter representing the strong T dependence of k on primary data, i.e., $k \propto T^{-(3+n)}$ where $-n$ is the functional dependence as shown in Fig. 2, and the additional -3 in the T exponent consists of two inverse powers which arise in the conversion from presssure to concentration and one in the dependence of the flow velocity on T. Error bars are not indicated in the Figs. 2 and 3, because they

would clutter the plots, which each contain all of the data for seven M-gases in $\log k$ vs. $\log T$ from (Fig. 2) and in Arrhenius form (Fig. 3). The approximate total length of such error bars (single standard deviation, including an estimate of systematic errors) would be about 0.08 (±0.04) in $\log k$ at 295°K and 0.15 (±0.075) at 77°K.

Table I also lists rate constant ratios, k^M/k^{H_2}, which show a relatively small range at 295°K, (from 0.87 for He to 2.41 for SF_6), but much larger ranges at 77°K (0.65 for He to 4.0 for CH_4) corresponding to the increasing negative temperature dependence of k^M in the order $He < H_2 < Ar < CH_4 < N_2 < SF_6 < CO_2$. This sequence is presented in the two parametric forms in Table II, i.e., as n from linear fits $k \propto T^{-n}$ in Fig. 2, and E from linear fits $k \propto \exp(+E/RT)$ in Fig. 3. The magnitude and range of these parameters, i.e., n from 0.4 to 2.27 and E (the *negative* Arrhenius activation energy) from 0.1 to 1.0 kcal mole^{-1}, will be discussed below. It should be noted (a) that the T^{-n} dependence gives some-

TABLE I

Listing of all measured recombination rate constants k^M as a function of temperature

M	T (°K)	$k_r{}^M \times 10^{33}$ (cm^6 sec^{-1})	Number of experiments	k^M/k^{H_2}
H_2	298	8.1 ±0.4	>200	
H_2	275	8.3 ±0.5	7	
H_2	253	9.4 ±0.3	10	
H_2	231	9.8 ±0.8	8	
H_2	210	10.5 ±0.9	10	
H_2	200	11.1 ±0.2	8	
H_2	180	11.4 ±0.2	8	
H_2	160	12.0 ±1.0	12	
H_2	140	13.3 ±0.9	7	
H_2	120	15.4 ±1.6	8	
H_2	77	18.5 ±2.2	85	
He	298	7.0 ±0.4	38	0.87±0.06
	77	12.0 ±1.5	41	0.65±0.09
Ar	298	9.2 ±0.6	24	1.14±0.09
	77	27.4 ±4.6	33	1.48±0.30
N_2	295	9.1 ±0.5	25	1.13±0.08
N_2	178	21.1 ±1.5	12	1.80±0.13
N_2	77	55.0 ±5.0	16	2.97±0.44
CH_4	295	15.3 ±0.8	17	1.89±0.13
CH_4	181	34.1 ±3.4	12	2.92±0.41
CH_4	77	73.8 ±9.9	18	3.99±0.75
CO_2	295	16.36±0.8	23	2.02±0.14
CO_2	255	19.67±1.0	12	2.21±0.16
CO_2	230	23.8 ±1.9	8	2.45±0.17
CO_2	222	30.0 ±2.8	12	2.86±0.30
CO_2	218	27.8 ±2.3	18	2.68±0.29
CO_2	208	33.3 ±3.5	12	3.30±0.23
CO_2	197	37.0 ±2.3	12	3.22±0.23
CO_2	175	53.2 ±3.7	10	4.47±0.38
SF_6	295	19.5 ±0.9	12	2.41±0.17
SF_6	161	57.1 ±3.4	8	4.24±0.31

what more linear fits, and (b) that any non-linearity in either plot is in the direction of decreased T dependence (smaller n or E) at the low end of the T range.

Discussion

The discussion is subdivided into three sections. The first presents a comparison with other published results at or near 300°K. The second deals with the recombination mechanism both in terms of the relative importance of energy transfer and radical molecule complex (or chaperone) routes

and in the assessment of quantum and classical effects. The last section attempts to correlate our results with those of high temperature studies.

Comparison with Other Results

In spite of the large number of early papers on H-atom recombination near 300°K, only a few of the most recent studies need be considered, mainly because in the older studies experimental conditions were not so chosen as to minimize the occurrence of several simultaneous atom loss processes. For k^{H_2} at 295°K our highly reproducible value of $(8.1\pm0.4)\times10^{-33}$ cm^6 sec^{-1} may be compared with 9.4 ± 1.4 by Larkin and Thrush,[11] and with 3.7 ± 0.5,[12] 4.4 ± 0.7,[13] and $(5.8\pm0.7)\times10^{-33}$ cm^6 sec^{-1}[14] by Bennett and Blackmore in three different studies. For k^{Ar} at 295°K, our $(9.2\pm0.6)\times10^{-33}$ cm^6 sec^{-1} is to be compared with 6.2 ± 0.7 by Larkin and Thrush,[11] 7.5 ± 1.1 by Bennett and Blackmore,[13] and 7.7 ± 0.6 by Azatyan et al.[15] Similarly, for k^{He} our value of $(7.0\pm0.4)\times10^{-33}$ cm^6 sec^{-1} is to be compared with 5.5 ± 0.8 by Bennett and Blackmore[13] and 10.0 ± 0.8 by Azatyan et al.[15] For the other M gases reported here, only the work of Bennett and Blackmore[13] is available for comparison. This comparison of relative efficiencies is summarized in Table III, normalized to k^{H_2}, all at or near 295°K. Agreement ranges from poor to fair. It is particularly disconcerting to find poor agreement among these rate constant ratios, where systematic errors should have cancelled, as in the case of k^{Ar}/k^{H_2} between Larkin and Thrush[11] and our work, even when there is good agreement on the value of k^{H_2}. With the more extensive results of Bennett and Blackmore[13] there is good agreement for N_2, CH_4 and possibly CO_2, but poor agreement for He and Ar. It should be noted, however, that their rate constants are all in-

TABLE II

Temperature dependence parameters n and E for k^M

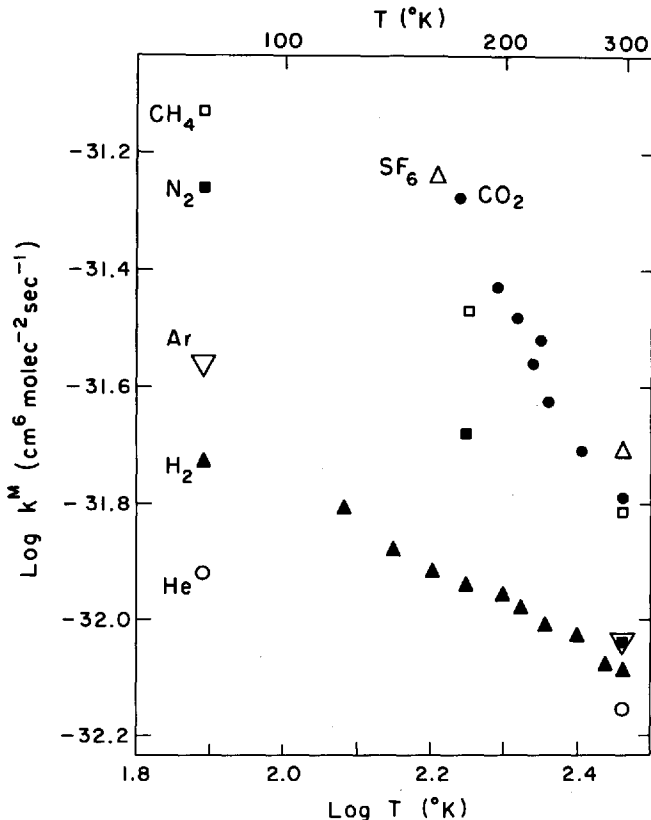| M	n	E (kcal mole^{-1})
He	0.40	0.11
H_2	0.60	0.17
Ar	0.81	0.23
CH_4	1.2	0.30
N_2	1.33	0.35
SF_6	1.8	0.76
CO_2	2.27	1.04

FIG. 2. Plot of log k^M vs log T for all M.

explicably low and that the flow tube conditions of their study, viz., 50 to 250 Torr pressure, probably preclude the simple analyses which invoked one-dimensional plug flow and thus require re-interpretation in view of complex and variable diffusion effects.

Except for Larkin and Thrush's[11] measurements of k^{Ar} at 213, 293, and 349°K which correspond to $n = 0.68$, in good agreement with our $n = 0.81$, the present work represents the only experimental study of the temperature dependence near 300°K. Figures 2 and 3 indicate that the T^{-n} functional form is somewhat better obeyed than an Arrhenius expression and may therefore be

used for moderate extrapolation. It is also evident from the values of k^M/k^{H_2} in Table I and from the corresponding n values in Table II that the magnitudes and temperature dependences of these ratios are inversely related, i.e., that a relatively large ratio, say, $k^{CO_2}/k^{H_2} = 2.02$ at 295°K, has a $T^{-(n_{CO_2}-n_{H_2})} = T^{-1.67}$ dependence which would make k^{CO_2} equal to k^{H_2} at about 450°K and smaller than k^{H_2} beyond that temperature. Values of this cross-over temperature, $T_C{}^M$, in the order of M in Table III, are 590, 550, 340, 650, 450, and 580°K. Although long extrapolations are clearly suspect, it is interesting to note that our results would predict a k^{N_2}/k^{H_2} ratio of
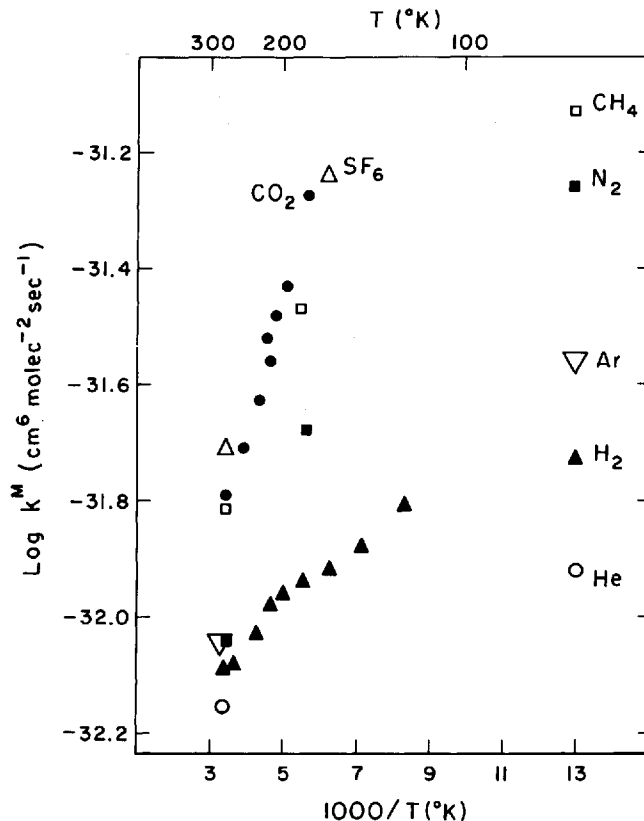
FIG. 3. Plot of log k^M vs $1/T$ for all M.

0.4 at 1200°K, in qualitative accord with some flame studies,[1] and a k^{Ar}/k^{H_2} ratio of 0.7 at 3000°K, in similar accord with some shock tube studies.[1] The limitations and pitfalls of this procedure will be discussed further in the last section.

Mechanism and Theory

The excellent success of the most recent *ab initio* calculation of the recombination by Whitlock *et al.*,[9] for $M = H_2$, He, and Ar, who invoke the ET mechanism, i.e., the collisional stabilization of quantum-mechanical resonances which are populated by tunnelling through the rotational

TABLE III

Relative efficiencies of M at 295°K

$M = H_2$	1	1	1
He	1.3		0.87
Ar	1.7	0.66	1.14
N_2	1.1		1.13
CH_4	1.7		1.89
CO_2	1.6		2.02
SF_6			2.41
Ref.	12	10	This work

barrier, suggests that this represents the major reaction path for very simple M below 300°K. In this calculation, the stabilization cross sections and rate constants of the resonances are computed from exact, three-dimensional, classical trajectories using the best available potential parameters. Because of the very weak H–M interactions (well depths of about 12, 28, and 95 cal/mole for He, H_2, and Ar), the RMC mechanism does not seem to contribute significantly to the recombination even at temperatures well below 300°K, and the negative temperature dependence of k^M appears to be largely due to the weak, long-range, attractive interaction in the stablizing collisions of the resonances with M. The fact that k^M/k^{H_2} ranges only from 1.13 to 2.41 at 295°K for the other four M; that n (or E) is only moderately larger for these M than for He, H_2, and Ar, with the possible exception of CO_2 which might have been expected to show a stronger interaction; and that there is no increase in n (or E) with decreasing temperature, for N_2 and CH_4 to 77°K and for CO_2 to 175°K, points to a comparably small contribution of the RMC channel for these larger and more complex M, again with the possible exception of CO_2. It is clear, moreover, that if the RMC path is unimportant at and below 300°K, it will remain so at higher temperatures where weakly bound H–M complexes are less likely to be present.

Originally, Roberts et al.,[8] had suggested that rotational relaxation was the principal route by which orbiting resonances were deactivated. The most recent trajectory calculation has shown, however, that the process involves simultaneous vibration and rotation transitions which may result in a more constant temperature dependence over a wider temperature range.

At temperatures well above 300°K, additional effects must be considered: (a) recombination via shorter-lived collision complexes above the rotational barrier, (b) re-dissociation of bound states, and (c) non-equilibrium effects. These should result in diminishing the temperature dependence and reducing the range of the M-effect. An extension of the resonance theory and synthesis with the classical phase space theory may soon be able to make good predictions over a wide range of T and M. In summary, it is our present view that for the seven M studied so far, the recombination proceeds almost entirely by the ET mechanism and that quantum effects predominate at temperatures below 300°K. It is clear, of course, that a complete description of the recombination–dissociation process is incredibly complex and requires the knowledge of a nearly infinite set of T-V-R collisional transition probabilities. It is equally clear that the recombina-

tion process at low temperatures involves an infinitesimally small subset of this vast array, i.e., the "action" is all very near the dissociation limit and there is no sense discussing H_2 dissociation near 300°K. Now, as there is nearly universal agreement among theorists and experimenters alike that the equilibrium constant does hold (after an induction period) it seems to us that the total process is better visualized and described from the recombination side in which, both experimentally and theoretically, there are only relatively slight changes with T as long as D/RT is large, say, >20, i.e., $T<2500°K$. It amounts perhaps to an invocation of the reasonableness of the Almighty to predict that the recombination rate constant will change smoothly and slowly over that entire temperature range, i.e., that neither the additional V–R levels nor the detailed collisional transition probabilities are going to produce strong gyrations. The temperature-dependent yardstick ought then to be one simply tied to thermal energy, kT, and not a fixed ϵ, i.e., the k^M vs. T dependence ought to be and is better represented as T^{-n}. It is unfortunate, therefore, that the vogue of representing dissociation rate constants of diatomics by Arrhenius expressions with $E<D$ has forced recombination rate constants into an equivalent mold which, although perhaps justified at very high T, is misleading below about 2500°K.

Correlation with High Temperature Results

In view of the preceding discussion we would expect the following qualitative behavior of k^M at higher temperatures: (a) Smooth connection and continuation with the low temperature values; (b) Decrease of the higher n or E values presented here at low T to a common range, perhaps around $n\sim0.5$ to 1 at high T, as specific long-range H_2^*–M interactions become less important; (This does not include the M = H case which is not treated here and which does include important RMC contributions). In applying these notions to the temperature dependence of k^{H_2} using the summary plot on p. 264 of the compilation of Baulch et al.,[1] we find gratifying agreement. A line through our data and through most of the recent shock tube values has a log k vs. log T slope of 0.6, exactly the same n as ours. Three flame results at 1200 to 1800°K seem to be factors of 3 to 10 too high, but the study of Dixon–Lewis et al.,[16] at this symposium re-interprets and corrects some of these values to give 4.7×10^{-33} cm^6 sec^{-1} at 1800°K (including, however, contributions due to M = N_2 and H_2O) which lies only 70% above the line $k^{H_2} = 8.1 \times 10^{-33} (T/300)^{-0.6}$. Dixon–Lewis et al.,[16] prefer the

Arrhenius expression 4.1×10^{-33} exp(0.5 kcal/RT) but that expression is much too steep at low T and probably too flat above 2000°K.

For k^{Ar} the spread among the published values from flame and shock tube work still covers a full order of magnitude. The line through our points and extrapolated to high temperature, i.e., a $T^{-0.8}$ dependence, passes approximately through the center of this spread. An evaluation of the high temperature data is out of place here.

Results for k^{N_2} are scattered and inconclusive. Some experimental analyses which put $k^{\text{N}_2}/k^{\text{H}_2}$ at around 0.1 are probably incorrect, and more recent flame and shock tube studies have reported $k^{\text{M}}/k^{\text{H}_2}$ and $k^{\text{M}}/k^{\text{Ar}}$ ratios nearer unity. The qualitative picture which is likely to emerge involves widely differing temperature coefficients at low temperatures leading to some crossovers and a general convergence of k^{M} at moderately high temperatures except for those M which have a strong, chemical interaction with H. The most pressing experimental problems for the near future would seem to be (a) extension of flow tube work to somewhat higher temperatures for a few M such as H_2, Ar, N_2, and CO_2, and (b) collection of accurate data, perhaps by Lyman-α absorption or fluorescence methods, at the *low* end of the shock tube domain for some of these same M.

Acknowledgment

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COMMENTS

W. Forst, Université Laval, Canada. Professor Kaufman's surmise that there might result a reversal of the order of M-efficiencies upon a substantial change of temperature, is a very interesting one, which has also occurred to us in connection with our calculations on hydrogen peroxide (see preceding paper No. 66). Although our calculations refer to a reaction that is an inverse of that considered by Prof. Kaufman (dissociation instead of recombination), and involves a much more complicated molecule, the results may be of some interest.

In our work, the primary calculated parameter is $k_0^\dagger/k_0$, the ratio of non-equilibrium and equilibrium low-pressure unimolecular rate constants for dissociation (the notation here is that of paper No. 66), which depends on the transition probability model and the average amount of energy

transferred per collision, $\langle \Delta E \rangle$. Specifying a given M means specifying $\langle \Delta E \rangle$ and the transition probability model. We find that over a small ($\sim 200°K$) temperature range (around $700°K$), $\ln(k_0^\dagger/k_0)$ vs $1/T$ is linear, and the straight lines for various models and various $\langle \Delta E \rangle$ do not cross, indicating that within this temperature range the order of M-efficiencies is preserved. *Linear* extrapolation of these straight lines to $2000°K$ reveals a few crossings of lines, which could be interpreted as reversal of M-efficiencies. However, it turns out that such a linear extrapolation is unjustified, because over a sufficiently large temperature range ($\sim 1000°K$) $\ln(k_0^\dagger/k_0)$ vs $1/T$ is appreciably *non-linear*; in other words, $k_0^\dagger/k_0$ has a non-Arrhenius temperature dependence [this can be seen also from the approximate analytical solution for $k_0^\dagger/k_0$ given in Eqs. (3) and (5) of paper No. 66]. Therefore any conclusions regarding possible reversal of M-efficiencies that are based on linear extrapolation of Arrhenius plots well outside the temperature range of the actual experiments must be viewed with suspicion. Although we have not yet done extensive calculations over a large temperature range, we think that a reversal of M-efficiencies would be the exception rather than the rule.

Authors' Reply. We can only reiterate some of the points made in the paper: (a) A surprisingly small temperature extrapolation is required to reach the "cross-over" temperature, e.g., $150°K$ (from $300°$ to $450°K$) for CO_2 versus H_2, and it is *not* an Arrhenius extrapolation but the very much milder T^{-n} extrapolation for the recombination rate constants. A rather sharp change in $n_{CO_2}-n_{H_2}$ would therefore be required to avert the cross over, but we quite agree that a gradual decrease in this quantity is physically appealing, i.e., the notion that the weak, long-range attractive forces in the CO_2-H_2 collisions become less important at higher collision energies.

(b) We would again urge everyone not to make such comparisons in the dissociation mode, where these tiny differences are totally submerged by the tremendously strong energy dependence of that process, but to apply the equilibrium constant (whose temperature dependence is also non-"Arrhenius" over wide temperature ranges) before making such comparisons. Speaking as experimentalists, we would expect the errors in the measured dissociation rates and possibly also in the thermodynamic properties to make a meaningful comparison with theory for such small effects virtually impossible.

♦

G. Dixon-Lewis, University of Leeds, England. Results for individual chaperon molecules at this level of reproducibility are indeed welcome, and they in turn allow more detailed analysis than has hitherto been possible, of recombination results in more complex systems. For example, the recombination results of Halstead and Jenkins[1] in the burnt gas of fuel-rich H_2-N_2-O_2 flames give an average k_{H+H+M} 1.73×10^{15} cm^6 $mole^{-2}$ sec^{-1} at $1800°K$, where M is a mixture of mole fraction composition $X_{N_2} = 0.524$, $X_{H_2} = 0.246$ and $X_{H_2O} = 0.230$. The present paper gives $k_{H+H+H_2} = 9.2 \times 10^{16}$ $T^{-0.6}$. If k_{H+H+N_2} is assumed to have the same temperature dependence, with a value of 3.3×10^{15} at $300°K$, then at $1800°K$ we have $k_{H+H+H_2O} = 3.8 k_{H+H+H_2}$. If on the other hand, as suggested in the paper, a $T^{-1.3}$ dependence is assumed for k_{H+H+N_2}, then $k_{H+H+H_2O} = 5.6 k_{H+H+H_2}$ is found.

REFERENCE

1. HALSTEAD, C. J. AND JENKINS, D. R.: Combust. Flame *14*, 321 (1970).