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NEUTRAL REACTIONS INVOLVING

HYDROGEN AND OTHER

MINOR CONSTITUENTS

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Neutral Reactions Involving Hydrogen and other Minor Constituents*

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Abstract

Experimental laboratory work is reviewed for the kinetics of 21 neutral, elementary reactions involving H, OH, HO_2, H_2, CO, N_2O, CH_4, and Na.

Introduction

Five years ago, at the Berkeley Symposium, this author presented a review of laboratory studies of relevant neutral reactions involving hydrogen (1). The present paper will attempt to bring that review up to date, and it will also briefly discuss the reactions of certain other minor constituents, not previously covered, at the suggestion of the organizers of this Symposium. It will not present, specifically, work done at the author's laboratory, and so is likely to be a drab recitation of experimentally measured rate parameters. The seemingly chaotic diversity and corresponding lack of clear trends among such rate parameters is, of course, a consequence of the greater inherent complexity of neutral reactions whose cross sections are generally smaller, energy barriers larger, interactions weaker, and intermediate states less predictable than those involving electrons or ions. The lively progress of fundamental rate theory (2) during the last few years will in general not be reflected in this review. The day when the detailed course of most elementary reactions will be open to investigation by single-collision methods (e.g. crossed molecular beam) in addition to the varied arsenal of bulk methods (with increasing sophistication of specific quantum state analysis) is unfortunately
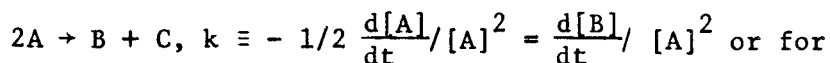
not yet at hand - except for alkali atom reactions - but, hopefully, it is not far

off. Until then, we must rely on chemical kinetic information obtained by various

methods such as discharge-flow, flash photolysis, steady photolysis, high temperature

kinetics and mechanism, flame sampling, shock-tube, and others. For the purpose of this

Symposium where the interest centers on reactions of simple atomic species at

temperatures from about 200 to $1000^{\circ}K$, the discharge-flow method has become the most

widely used. Its many variants include formation of reactive species in glow

discharges, in thermal sources, or by chemical reaction of energetic precursors;

reaction with added molecules along a cylindrical flow tube or in stirred-flow

reactor; and detection by measurement of a simply related chemiluminescent emission,

by wire calorimetry, optical absorption, e.s.r. absorption, mass spectrometry, gas

titration of the reactive species, or by other methods. As one reviews the

published results of such experiments critically, one should keep in mind all

inherent limitations or assumptions which will tend to reduce the accuracy of their

results. For example, the experimental errors introduced in the measurements of

pressure in the 0.1 to 10 Torr range, of all flow rates (properly reduced to cm^{3}

sec^{1} N.T.P. or particles sec^{-1}), and of the geometry of the flow tube or reactor, -

and thereby the elapsed time-are likely to result in a minimum probable error of about

10% in the resultant rate constant. Next, major uncertainties arise from the

oversimplification of the gas flow and from uncontrolled side reaction. Thus, for

relatively slow reactions, concurrent surface recombination is always a serious

problem: and for very fast reactions whose rate often can not be reduced by lowering

reactant concentrations because of detector sensitivity, the flow velocity is likely

to be high (0.2 to 1 x 10^{4} cm sec^{-1}) which complicates the reactant mixing problem,

impedes the establishment of Poiseuille flow, and introduces axial pressure

gradients. Probable errors of 10% due to these causes would seem to be conservative

estimates in most cases. Finally, there are the errors associated with the

method of detection. These are particularly serious when the absolute

concentration of a reactive species must be known as in the calculation of bimole-
cular rate constants for the reaction involving two such molecules. In such cases,
uncertainties in the optical or e.s.r. absorption coefficient, discrimination
effects in mass spectrometric analysis, unknown detection efficiency and diffusion
effects in probe calorimeters, and titration errors (especially overtitration) in
chemiluminescent titrations, will add further errors which will usually amount
to at least 10 to 20%. It is clear, of course, that in any one series of
measurements most of these errors will tend to remain fairly constant, and that
therefore the average deviation from the mean in such a series is likely to be much
smaller than the true probable error. This rather obvious reminder of the difference
between precision and accuracy would seem to be out of place in such a review, were
it not for the alarming rise in the claimed accuracy of many reported kinetic
parameters. Thus, claims of a probable error (single standard deviation) in a
rate constant of less than about $\pm 15\%$ should in most cases be disregarded. As an
example, one may cite one of the most easily measured rate constants by discharge-
flow techniques, the recombination rate constant for $0 + NO + O_2 \rightarrow NO_2 + O_2$ - which
is not a subject of this review - for which six separate investigations have reported
values of 5.1, 5.1, 6.0, 6.0, 7.6, and 8.0 x 10^{-32} cm^6 $molecule^{-2}$ $sec,^{-1}$, even
though this is a pseudo first order process in which the concentrations of NO and
O_2 are easily measured and remain constant and that of 0 therefore need not be
known in absolute magnitude.

II. Review of Recent Rate Data.

The writing of this review was much aided by other recent summaries,
especially by the excellent evaluation of kinetic rate data of Schofield (3) and
by other review articles (4,5,6). Reactions will be discussed in the approximate
order of this author's earlier review (1), beginning with reactions of H, followed
by OH, HO_2, H_2, and H_2O, and ending with a few reactions of CO_2, N_2O, CH_4, and of
Na. Molecular units (cm^3 $molecule^{-1}$ sec^{-1} or cm^6 $molecule^{-2}$ sec^{-1}) will be used

throughout, and should be assumed to apply when not specified. Specific rate constants are reported, i.e. for the reaction

$2A \rightarrow B + C$, $k \equiv - 1/2 \frac{d[A]}{dt}/[A]^2 = \frac{d[B]}{dt}/[A]^2$ or for

$2A + M \rightarrow A_2 + M$, $k \equiv - 1/2 \frac{d[A]}{dt}/[A]^2[M] = \frac{d[A_2]}{dt}/[A]^2[M]$.

For each reaction, the energy change at absolute zero temperature, ΔE_o^o, will be given in units of kcal mole^{-1}, based on thermochemical data from the JANAF tables (7). Where this author is unaware of new work since his earlier review, that recommended value will be repeated without discussion for increased usefulness. Lastly, apologies are again in order for possible crimes of omission or commission.

A. Reactions of H-atoms

1. $H + H + M \rightarrow H_2 + M$, $\Delta E_o^o = - 103.26$
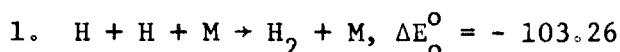
This reaction is not of aeronomic interest. It continues to be studied over a wide temperature range, because it is the most important test case of theory and experiment of atom recombination. Larkin and Thrush (8) studied the T dependence (213 to 349°K) for M = Ar and found $k = 1.2 \times 10^{-32} (273/T)^{0.7}$, in fairly good agreement with the theory of Benson and Fueno (9), although the latter predicts a weaker T dependence ($\sim T^{-0.3}$ for a Lennard-Jones potential for H + H collision complexes).

The extensive work at high T by shock tube techniques can not be reviewed here. Sutton (10) finds a T^{-1} dependence between 2800 and 4500°K for M = H_2, and his k extrapolates well to discharge-flow data near 300°K. His k for M = H is about ten times larger. Hurle (11) is in good agreement with Sutton for M = H_2, but reports a very much larger k for M = H, with a very large negative T dependence, T^{-7}, between 4000 and 6000°K. Such a value is clearly not extrapolatable to 300°K, and Hurle is reported to have seen k come to maximum value near 3000°K and to appear to decrease again at lower T (12). Rosenfeld (12) has suggested an explanation for this interesting observation. More experimental work is needed, especially in an intermediate T range. Although there is qualitative

agreement on the relative efficiency of different M, i.e. $Ar < N_2 < H_2O < H_2 < H$, there remain wide discrepancies in their exact magnitude.

$$2. \quad H + O_2 + M \rightarrow HO_2 + M \qquad\qquad \Delta E_o^o = -45.9$$

Two studies near $300°K$, one using chemiluminescent (13) and the other probe (14) detection have shown this to be a "normal" three-body atom-molecule recombination with a k of $3 \pm 1 \times 10^{-32}$ (M = Ar) and a ratio of about 20 for $k^{H_2O}: k^{Ar}$. From the M-effect on the second explosion limit of $H_2 - O_2$ explosions near $800°K$, similar relative M-efficiences are obtained which place He and O_2 near Ar, N_2 1.5 to 2 times larger, H_2 3 times larger. Schofield (3) combined most available rate data to obtain $k = 3 \times 10^{-32} (273/T)^{1.3}$ which is likely to be approximately correct although the $T^{-1.3}$ dependence is weaker than that of several similar recombinations.

$$3. \quad H + O_2 \rightarrow OH + O \qquad\qquad \Delta E_o^o = 16.63$$

The reaction is sufficiently endothermic to be of no direct importance. There is no experimental information on the interesting possibility of a forward reaction with O_2, $X^3 \Sigma_g^-$, v" ≥ 4 or with O_2, $a^1 \Delta_g^+$ or $b^1 \Sigma_g^+$. From the very large k of the reverse reaction, $5 \pm 2 \times 10^{-11}$, (1), and the equilibrium constant, 21 exp (16.8/RT), a value of 1×10^{-9} exp (-16.8/RT) is obtained if the reverse reaction k is assumed to be T independent. If the reverse reaction produces substantial vibrational excitation in O_2, the above "thermal" k would be too large. The very large pre-exponential factor indirectly supports such a possibility.

$$4. \quad H + NO + M \rightarrow HNO + M \qquad\qquad \Delta E_o^o = -48.6$$

Further work on this reaction since the last review included measurement of k at $293°K$ for six M as well as measurement of the relative M effect in the concurrent chemiluminescent reaction to form HNO* (15). For M = H_2, k is now found to be 5.7×10^{-32}, compared to 3.8×10^{-32} in the earlier work of the same laboratory (16), and the relative efficiency of M in the recombination, normalized to M = H_2 are: He - 0.47, Ar-0.54, CO_2 - 1.1, N_2O - 1.2, SF_6 - 1.9, H_2O - 3.3. The formation of HNO* was found to depend on M in a similar manner. The further bimolecular reaction, $2 HNO \rightarrow N_2O + H_2O$ was investigated by Clyne (17) who placed

a lower limit of 0.5×10^{-16} on its rate constant, and by Kohout and Lampe (18) who find $k = 6.7 \pm 10^{-16}$ in a photolysis mass spectrometer study.

5. $H + NO_2 \rightarrow OH + NO$ $\qquad \Delta E_o^o = -29.5$

No new work is available. The direct measurement of Phillips and Schiff (19) at $300^o K$ gave $4.8 \pm 0.5 \times 10^{-11}$, and an indirect one by Rosser and Wise (20) gave much the same value near $500^o K$. The latter value was misread by Schofield (3) who reported it as 2×10^{-9}. Further unpublished work at this author's former laboratory has confirmed the earlier conclusion that there is very little if any vibrationally excited OH formed in the reaction.

6. $H + O_3 \rightarrow OH + O_2$ $\qquad \Delta E_c^o = -77.1$
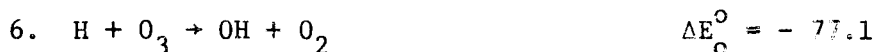
This reaction was extensively discussed in the earlier review (1). No new data are available on its rate constant, $2.6 + 0.5 \times 10^{-11}$ at $300^o K$ as reported by Phillips and Schiff (19). Further work in the author's former laboratory has confirmed the formation of vibrationally highly excited OH as a major reaction product and has provided information on its collisional deactivation by various added gases. Anlauf, Macdonald, and Polanyi (21) have recently studied the infrared chemiluminescence of this reaction at pressures down to 10^{-4} Torr under conditions where $OH^{\ddagger}$ would either react or be deactivated to $v'' = 0$ at the wall of the reactor. The infrared emission indicated a highly non-Boltzmann distribution of $OH^{\ddagger}$ with increasing populations up to $v'' = 9$, the highest available level, and about 80 to 85% of all molecules in $v'' \geq 4$ if the populations in $v'' = 0$ to 2 are estimated by extrapolation. This result is in good agreement with the earlier u.v. absorption work (1) in which only molecules with $v'' = 0$ and 1 were observed. The various fates of $OH^{\ddagger}$ as a result of radiation, physical quenching, or chemical reactions were presented in the earlier review. The detailed course of its reaction with O_3 has been further clarified by DeMore (22) who showed that the reaction between $OH^{\ddagger}$ and O_3 may produce $H + 2 O_2$ via highly excited HO_2 after a single collision rather than only by two successive collisional processes, i.e.

$OH^{\ddagger} + O_3 \rightarrow OH + O_2 + O$, followed by $OH + O \rightarrow O_2 + H$ (1). This helps explain why the yield of OH, $v'' = 0$, does not increase strongly when very small concentrations of H are reacted with excess O_3.

7. $H + OH \rightarrow H_2 + O$ $\qquad\qquad\qquad$ $\Delta E_o^o = -1.9$

This rate constant is best obtained from its much studied reverse reaction for which three new values have been reported since the last review: 7×10^{-11} exp (-10.2/RT) (23), 2×10^{-11} exp (9.2/RT) (24), and 8×10^{-11} exp (-10.2/RT) (25) Combined with the equilibrium constant, $k = 0.44$ exp (1.87/RT), and using the larger activation energy, one obtains 3×10^{-11} exp (8.3/RT) which, although differing fairly substantially from the earlier recommended expression (1), does not yield very different rate constants near 300^oK.

8. $H + HO_2 \rightarrow 2OH$ $\qquad\qquad\qquad$ $\Delta E_o^o = -38.8$

8'. $H + HO_2 \rightarrow H_2 + O_2$ $\qquad\qquad\qquad$ $\Delta E_o^o = -57.3$

No new work is available. The earlier rough estimates of $k_8 \geq 3 \times 10^{-12}$ stand (1).

B. Reactions of OH.

9. $2 OH \rightarrow H_2O + O$ $\qquad\qquad\qquad$ $\Delta E_o^o = -16.7$

Since the earlier work (1) which reported $1.4 \pm 0.3 \times 10^{-12}$ at 300^oK (the quoted 2.8×10^{-12} referred to $-d[OH]/dt = k[OH]^2$, i.e. twice the specific rate constant) several other values have been published. Westenberg and deHaas (26) found $2 \pm 0.6 \times 10^{-12}$ by a similar method except for e.s.r. detection, and later work in the same laboratory (27) led to $2.6 \pm 0.25 \times 10^{-12}$. (The stated errors are single standard deviations calculated from the published data). Wilson and O'Donovan (28) recently re-analyzed Herron's (29) data on the CO + OH reaction and calculated $1.1 \pm 0.1 \times 10^{-12}$ for the OH + OH reaction. They then performed similar experiments which yielded $2.1 \pm 0.1 \times 10^{-12}$, but rejected both

in favor of their earlier 2.6 ± 0.25 x 10^{-12} (28). Several of these authors err

in claiming excessive accuracy as discussed in the introduction, i.e. they simply

report the average deviation from the mean of their calculated values, which is

sometimes as low as ± 3%. It is difficult to assess which of the two principal

measurements, 1.4 ± 0.3 x 10^{-12} by u.v. or 2.6 ± 0.25 x 10^{-12} by e.s.r. absorption,

is more reliable. Experimentally, the u.v. value has a slight edge, because it

averages OH over a shorter distance along the flow tube, permits its measurement

closer to the mixing point where OH is produced, and uses a better mixing device

for the parent H + NO_2 reaction. The u.v. method was also used to measure the

oscillator strength of the pertinent electronic transition, $^2\Sigma^+ - {}^2\pi$, and a result

$f_{o,o}$ = 7.1 ± 1.0 x 10^{-4} was obtained (30) in good agreement with the best direct

measurement of the radiative lifetime (31) which yields 8.0 ± 0.8 x 10^{-4}. The

effect of adopting the slightly higher f would be a proportional decrease in all

OH concentrations and an increase of k from 1.4 to 1.6 ± 0.3 x 10^{-12}. The higher

e.s.r. value, on the other hand, is supported by measurement of the ratio

$[O_2]_\infty / [CO_2]_\infty$ at large reaction times when the OH + CO reaction occurs concurrently,

even though this support is predicated on the correctness of the OH + CO rate

constant. Very likely, the correct k will lie somewhere between 1.4 and 2.6 x 10^{-11},

but exaggerated claims of high accuracy should be disregarded.

10. OH + O → O_2 + H ΔE_o^o = - 16.6

No further work is available. The earlier value of 5 ± 2 x 10^{-11} at 300°K

stands.

11. OH + O_3 → HO_2 + O_2 ΔE_o^o = - 38.3

DeMore's recent photolysis work (22,32) supports the earlier conclusion (1)

that ground-state OH does not react rapidly with O_3 (k ≤ 5 x 10^{-13}) whereas excited

OH from the H + O_3 reaction does so. No direct proof is available for the often

invoked chain decomposition of O_3 by this reaction followed by

HO_2 + O_3 → OH + $2O_2$, and such a scheme should not be postulated without proof.

With highly excited OH$^+$, the reaction proceeds to give H + $2O_2$ as previously
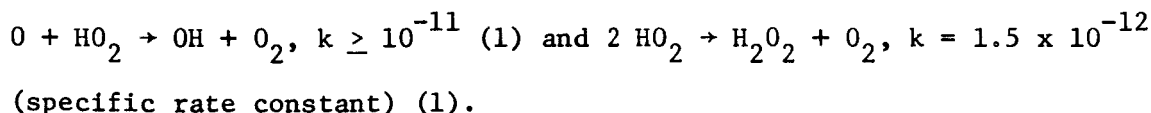
discussed.

12. $OH + HO_2 \rightarrow H_2O + O_2$ $\qquad\qquad \Delta E_o^o = -72.1$

The earlier recommendation of a fast reaction, $k \geq 10^{-11}$, on the basis of indirect information on HO_2 production, still stands.

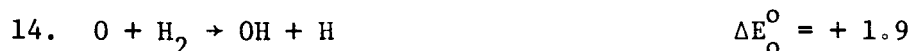13. $OH + H_2 \rightarrow H_2O + H$ $\qquad\qquad \Delta E_o^o = -14.7$

Two new measurements of this rate constant at 300^oK have been reported, both in good agreement with the earlier value of $7 \pm 2 \times 10^{-15}$ (1). Dixon-Lewis, Wilson, and Westenberg (27) find $6.5 \pm 0.5 \times 10^{-15}$ by e.s.r. and Greiner (33) $6.7 \pm 0.4 \times 10^{-15}$ by flash photolysis and kinetic spectroscopy. Combined with flame and shock tube data, this value has led to several Arrhenius expressions for k such as 6.3×10^{-11} exp $(-5.49/RT)$ (3), 1×10^{-10} exp $(-5.9/RT)$ (1), and 3.8×10^{-11} exp $(-5.2/RT)$ (27) which are also in close agreement over the relevant T range.

C. Reaction of HO_2

No new information is available for the reactions $0 + HO_2 \rightarrow OH + O_2$, $k \geq 10^{-11}$ (1) and $2 HO_2 \rightarrow H_2O_2 + O_2$, $k = 1.5 \times 10^{-12}$ (specific rate constant) (1).

D. Reactions of H_2

14. $0 + H_2 \rightarrow OH + H$ $\qquad\qquad \Delta E_o^o = +1.9$

Several new studies of this important reaction of ground-state oxygen, ^3P, have been reported, as noted above in the discussion of the reverse reaction. The rate expressions are:
7×10^{-11} exp $(-10.2/RT)$ (23), 2×10^{-11} exp $(-9.2RT)$ (24), and
8×10^{-11} exp $(-10.2/RT)$ (25). Combining the first two of these with the earlier
2×10^{-11} $(-9.4/RT)$ (34), Schofield suggested 2.1×10^{-11} exp $(-9.4/RT)$ (3). The most recent of these investigations, by Westenberg and deHaas (25) who use the discharge-flow method and e.s.r. detection, also indicates deviations from an Arrhenius expression at the low T end of their range $(350^o$K) which may be due to tunnelling. The higher activation energy of 10.2 kcal seems to be slightly

preferable, and an expression 7×10^{-11} exp (-10.2/RT) is recommended.

E. Reactions of CO and CO_2

As additional species are brought in for consideration and review, the number of possible reactions increases exponentially. Only very few of these reactions will be discussed, however, partly because of low aeronomic interest and partly because of the paucity of laboratory data. Moreover, all reactions of excited states are discussed elsewhere.

15. $OH + CO \rightarrow H + CO_2$ $\qquad\qquad \Delta E_o^o = -24.4$

Three recent measurements near $300^o K$ have shown that this reaction has a much smaller activation energy than heretofore believed. Thus, Westenberg and Fristrom (35) combined available kinetic data in 1964 to give the rate expression 1.2×10^{-11} exp (-7.7/RT), based in part on incorrect early discharge work (36).

Yet since then, all measurements have indicated that E<2 kcal. Herron (30) reported $8.5 \pm 3 \times 10^{-14}$ at $300^o K$ and derived 1.5×10^{-12} exp (-1.7/RT) by combination with explosion and flame data; Dixon-Lewis, Wilson, and Westenberg (28) obtained 1.9×10^{-13} at $300^o K$ and derived 5.0×10^{-13} exp (-0.6/RT); Greiner (34) obtained 1.5×10^{-13} at $300^o K$; and Wilson and O'Donavan (29) also obtained 1.5×10^{-13} although they prefer the somewhat higher 1.7×10^{-13} based on the earlier measurement of reaction 9. A three parameter expression for this rate constant has also been proposed (28) but is surely not warranted in view of the large spread of nearly an order of magnitude in the high T data. A compromise of 9×10^{-13} exp (-1.0/RT) is suggested, albeit without special evidence.

The reverse reaction is endothermic and therefore quite slow. Using the expression 2.3×10^{-3} exp (+24.7/RT) for the equilibrium constant over the range 300 to $1000^o K$, the reverse k is 4.0×10^{-10} exp (-25.7/RT). At $1000^o K$, the equilibrium constant is 620 which shows that the reverse reaction is not altogether negligible.

16. $O + CO + M \rightarrow CO_2 + M$ $\qquad$ $\Delta E_o^o = -125.75$

Our understanding of this simple recombination reaction is still in a most unsatisfactory state. There is general agreement that the reaction is at least two to three orders of magnitude slower than "normal" recombinations such as $O + NO + M$ or $H + O_2 + M$, and therefore difficult to study in low pressure flow systems. But there has been lack of agreement whether the process is of second or third order in the Torr pressure range, and whether it has a positive or negative T dependence. Clyne and Thrush (37) found no measurable reaction at $293^o K$ at a total pressure of 2 Torr and CO partial pressure up to 0.5 Torr, and placed an upper limit of 8×10^{-35} on the third order k. They also reported a second order chemiluminescent rate constant of 1×10^{-17} exp (-3.7/RT) for M = O_2, indicating small energy barrier. Mahan and Solo (38) claim the recombination to be second order to pressures as low as 0.2 Torr and report $k = 1.6 \times 10^{-14}$ exp (-4.0/RT) for the overall reaction and 2×10^{-13} exp (-9.5/RT) for the chemiluminescent reaction. The former value is almost four times as large as the above upper limit at 2 Torr and therefore inconsistent with it. Hartunian, Thompson, and Hewitt (39) studied only the chemiluminescent reaction in a glow-discharge shock tube and reported 1.6×10^{-18} exp (-2.5/RT) in fair agreement with ref. 37 and in good agreement with a value 0.5×10^{-18} exp (-2.5/RT) obtained by Myers and Bartle (40) from shock tube work near $3000^o K$. Avramenko and Kolesnikova (41) also reported the overall reaction to be second order with $k = 1.6 \times 10^{-13}$ exp (-3.8/RT), but this value gives much too high a k at $300^o K$ and is in strong disagreement with a recent measurement by Mulcahy and Williams (42) whose measured $O + CO$ rate is 100 times slower than the above at $456^o K$. In all, it seems likely that the reaction has a small energy barrier and is third order, in the few Torr pressure range, but a definitive experimental study has yet to be undertaken.

17. $H + N_2O \rightarrow OH + N_2$ $\Delta E_o^o = -62.8$

The neutral chemistry of N_2O is unlikely to be of much importance in aeronomy because all its reactions involve fairly large energy barriers. This is true of the reaction $O + N_2O \rightarrow 2NO$ whose energy of activation is near 25 kcal and it also applies to this reaction although to a lesser extent. The $H + N_2O$ reaction was investigated indirectly by Fenimore and Jones (43) at 1260 to 1780^oK by flame probe methods. These authors reported 7×10^{-10} exp $(-16.3/RT)$, but this result was based on the high value of the activation energy for reaction 13, and the rate expression should therefore now be changed to 1.3×10^{-10} exp $(-11.3/RT)$. This is in fair agreement with more recent measurements by Dixon-Lewis, Sutton, and Williams (44) whose k's indicate a similar activation energy of 10.1 kcal but are smaller in magnitude. Schofield (3) suggests the rate expression 5×10^{-11} exp $(-10.8/RT)$ as a mean of the available data. Because of slowness of this and other N_2O reactions and because of the low concentrations of reactants it seems clear that its photochemistry will be of much greater importance than the above collisional processes.

18. $H + CH_4 \rightarrow CH_3 + H_2$ $\Delta E_o^o = -2.8$

The above remarks are applicable here. With the exception of the reaction with $O, {}^1D$, which is not covered in this review, all other neutral reactions of CH_4 of aeronomic applicability involve energy barriers and are likely to be slow compared with photoexcitation or dissociation. For the present reaction, the ΔE_o^o of 2.8 kcal calculated from the JANAF tables should probably be replaced by a value of -0.6 kcal based on Golden, Walsh, and Benson's (45) value for the energy of formation of CH_3. Twelve investigations of this reaction are cited in a recent review (4). Reported activation energies range from 4.5 to 15.1 kcal and pre-exponential values from 10^{-14} to 5×10^{-10}, but there is much better agreement on the absolute value of k than is indicated by this large spread. Schofield (3) has combined the data of seven of these studies in an Arrhenius plot and reports

6.7×10^{-11} exp $(-11.6/RT)$ which indicates that the reaction is negligibly slow near near $300^{\circ}K$.

19. $OH + CH_4 \rightarrow H_2O + CH_3$ $\qquad$ $\Delta E_o^o = -17.6$

Similar considerations apply here regarding ΔE_o^o which is more probably -15.4 in view of the recent work on CH_3 (45). This reaction has been studied repeatedly by a variety of experimental methods, with reported activation energies ranging from 5.0 to 9.0 kcal. Schofield's (3) analysis of most available data yields 1.2×10^{-10} exp $(-5.9/RT)$. In view of the very rapid reaction of OH with O, the steady-state OH concentration is probably very small, and the present reaction is of no importance.

20. $CH_4 + O \rightarrow CH_3 + OH$ $\qquad$ $\Delta E_o^o = -0.9$

ΔE_o^o is more probably $+1.3$ kcal (45). Several recent studies of this reaction over the T range 300 to $1000^{\circ}K$ are in surprisingly good agreement. Thus, Schofield (3) summarized the available data by the rate expression 5.3×10^{-11} exp $(-7.95/RT)$, where the specific investigations ranged only from 6.9 to 8.7 kcal in their activation energies. Since the time of that summary, two more studies have been published, both using discharge-flow e.s.r. methods: Brown and Thursh (46) obtain 1.2×10^{-11} exp $(-7.7/RT)$ and Westenberg and deHaas (25) report 2.8×10^{-11} exp $(-8.7/RT)$. The latter expression probably represents the most accurate work, and since it also covers a much larger T range than the former, it is to be preferred. It should be remembered that in this rate constant the subsequent reaction of CH_3 with excess O have been taken into account, i.e. the total O-atom decay rate constant is given by $4k$.

21. $Na + O_2 + M \rightarrow Na O_2 + M$
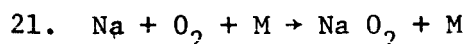
No value of ΔE_o^o is given for this reaction, because $Na O_2$ (g) is not listed in the JANAF tables. There exists a recent, indirect measurement of ΔE_o^o by McEwan and Phillips (47) of -65 ± 3 kcal, based on the approach to equilibrium of the present reaction in O_2- rich H_2-O_2-N_2 flames. Compared with the corresponding values of

-45.9 for HO_2, this seems unexpectedly high. These authors also report a value of 2.0 x 10^{-35} for the rate constant, surprisingly independent of T over the range 1380 to 2030°K. This is in fairly good agreement with an earlier measurement by Kaskan (48) of 0.8 x 10^{-33} obtained from flame work at 1 atm pressure in which the reaction order could not be established. Recently, the pressure dependence of this process was investigated by Carabetta and Kaskan (49) over the pressure range from 100 to 1520 Torr, and the third order dependence was verified. A rate constant of 0.83 x 10^{-33} was reported near 1500°K. With an assumed $T^{-1 \text{ to } -2}$ dependence this will lead to a range of 0.5 to 2.5 x 10^{-32} near 300°K, 200 to 1000 times smaller than similarly extrapolated results of Bawn and Evans (50) which are probably too large because of neglect of quenching of Na, ^2P, by N_2 as discussed by Blamont and Donahue (51). However, this discrepancy appears too wide to be bridged by correction of the diffusion flame data (50). The flame k's are smaller than one would expect for a fully allowed three-body process involving a large atom and a moderately electronegative molecule, they show no T dependence over a fairly large range, and they lead to an unreasonably large bond energy. Additional work at low T is needed.

To this author's knowledge, no experimental data are available on the kinetics of the reaction $NaO_2 + O \rightarrow NaO + O_2$ and $NaO + O \rightarrow Na + O_2$ If the recent Na - O_2 bond strength of 65 kcal is correct and the JANAF value of 71.2 for the Na-O bond strength is accepted, the former process is only about 6 kcal exothermic and the latter 46.8 kcal, only 1.7 kcal less than the excitation energy of Na, $^2P_{1/2}$. The many other exothermic reaction of Na-oxides with H or OH can not be discussed for lack of any laboratory information.

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