Thermal Decomposition of Nitrous Oxide. Comparison of Theory with Experiment

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Quantum-mechanical ab initio calculations show that the pressure-dependent unimolecular rate constant k_{uni} and the corresponding activation energy should remain pressure dependent over a range of pressures so wide that the second-order limit should not be attainable at any practical pressure. Available experimental data give qualified support to the calculations.

1. Introduction

Recent ab initio quantum-mechanical calculations[1] have provided values of the microcanonical rate constant $k(E)$ for the spin-disallowed decomposition into $N_2 + O(^3P)$ of N_2O molecules of specified energy E. The calculations show that the energy dependence of this $k(E)$ has two unusual features: (1) the reaction threshold is not sharp, meaning that at energy threshold $k(E)$ does not rise steplike fashion from zero to some large value (typically $\gg 10^3$ s^{-1}) but rises from zero to only $\leq 10^{-7}$ s^{-1}, and (2) $k(E)$ above threshold rises gradually but very strongly with energy, roughly as $\sim E^{18}$ (Figure 2 in ref 1).

As indicated in the preceding paper,[2] the consequences of this in a thermal system are twofold: the limiting high-pressure activation energy $E_{a\infty}$ is strongly temperature dependent below ~ 600 K (Figure 4 in ref 2), and the thermal pressure-dependent rate constant k_{uni} and the corresponding activation energy E_a show a pressure falloff that continues to exceedingly low pressures (see Figure 1-4 below). It appears, therefore, that the second-order limit of the thermal N_2O decomposition is unattainable at any practical pressure.

The purpose of this paper is to examine to what extent the unusual calculated energy dependence of $k(E)$ is borne out by experimentally measurable properties of the thermal N_2O reaction system, and how this might alter the interpretation of experimental results.

2. High-Pressure Limit

The recommended experimental value for the limiting high-pressure rate constant for N_2O decomposition is[3] $k_\infty = 1.3 \times 10^{11} \exp(-20850 \text{ cm}^{-1}/kT)$ s^{-1}, valid between 900 and 2100 K.

In the ab initio calculations of the rate constants $k(E)$, the principal uncertainty concerns the value of the spin-orbit coupling constant H^c_{ab}. A simple a priori estimate[1] of $H^c_{ab} \sim 46$ cm^{-1} leads to $k_\infty = 1.64 \times 10^{12} \exp(-20484.43$ cm$^{-1}/kT)$ s^{-1} at 900 K, i.e., a preexponential factor that is clearly too large. Since H^c_{ab} affects only the preexponential factor, this suggests that the value of the coupling constant must be smaller than 46 cm^{-1}, and we have presented an argument showing how such a reduction in H^c_{ab} might come about.[1] In the calculations that follow, we use $H^c_{ab} = 10.5$ cm^{-1}, with the result that the rate constants $k(E)$ reported previously are to be all multiplied by 0.052, which leads to

$$k_\infty = 8.53 \times 10^{10} \exp(-20484.43 \text{ cm}^{-1}/kT) \text{ s}^{-1} \quad (1)$$

at 900 K, and to $k_\infty = 8.64 \times 10^{10} \exp(-20491.14 \text{ cm}^{-1}/kT)$ s^{-1} at 888 K, which is substantially the same result. Compared with the recommended experimental value, the calculated k_∞ of eq 1 yields values about 16% too high at 888 K, and about 20% too low at 2000 K.

It should be emphasized that the adjustment of H^c_{ab} is, at this point, the *only* instance in the ab initio calculations of the rate constants $k(E)$ in which use is made of kinetic information. It merely scales the rate constants $k(E)$ but does not in any way affect their energy dependence. Thus, in particular, the calculated temperature dependence of the limiting high-pressure activation energy $E_{a\infty}$ remains the same as that shown in Figure 4 of ref 2, i.e., a predicted strong temperature dependence of $E_{a\infty}$ below ~ 600 K.

It would be most desirable to have experimental confirmation of this temperature dependence of $E_{a\infty}$. Unfortunately, since $E_{a\infty}$ has not been determined experimentally as a function of temperature below 900 K (in fact it would be difficult if not impossible to determine $E_{a\infty}$ at any temperature much lower than this), the calculated temperature dependence of $E_{a\infty}$ does not admit of direct experimental verification. One is therefore relegated to examine the pressure dependence of rate constants k_{uni} and of activation energies E_a for which experimental data do exist.

In the following, the experimental data will be compared with two series of calculations: (a) using theoretical ab initio $k(E)$'s ($H^c_{ab} = 10.5$ cm^{-1}) and discrete summations (eq 4, 7, and 10 in ref 2); in the interest of brevity, any property so calculated will be referred to as "exact", and the corresponding curves labeled "a"; (b) using $k(E)$'s obtained by inversion from eq 1, plus integrations over all energies (eq 3 and 5 in ref 2); properties so calculated will be referred to as "by inversion" and the corresponding curves labeled "b".

The reason for including calculation b is to provide a comparison with a more "traditional" interpretation, one where (1) $E_{a\infty}$ is assumed to be a constant at all temperatures, equal to 20 484 cm^{-1}, (2) threshold to reaction is at $E_{a\infty}$, i.e., substantially higher than in calculation a where it is at 14 135 cm^{-1}, (3) $k(E)$ rises at threshold steplike from zero to $\sim 10^8$ s^{-1} (ref 2, dashed line in Figure 1), and (4) $k(E)$ depends on energy as $\sim E^2$. Calculations a and b thus represent sharply contrasting properties at the microscopic level and provide two radically different models of the reacting system, although they both give the same k_∞ above 900 K.

3. High-Pressure Falloff at 888 K

Johnston[4] has analyzed data of five different experimental studies of the N_2O decomposition done in static systems between 841 and 1052 K and corrected them for

(1) A. J. Lorquet, J. C. Lorquet, and W. Forst, *Chem. Phys.*, **51**, 253 (1980).

(2) W. Forst, *J. Phys. Chem.*, preceding paper in this issue.

(3) D. L. Baulch, D. D. Drysdale, and D. G. Horne, "Evaluated Kinetic Data for High Temperature Reactions", Vol. 2, Butterworths, London, 1973. See also K. M. Pamidimukkala, A. Lifshiftz, G. B. Skinner, and D. R. Wood, *J. Chem. Phys.*, **75**, 1116 (1981).

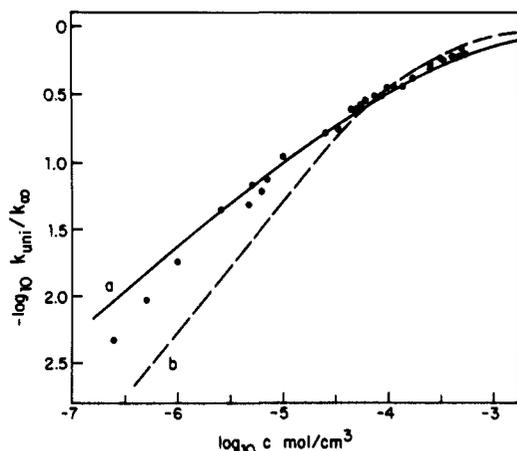(4) H. S. Johnston, *J. Chem. Phys.*, **19**, 663 (1951).

Figure 1. Pressure dependence of rate constant for N_2O decomposition at 888 K. Black dots: composite experimental data as corrected for heterogeneity by Johnston (ref 4, Table IV). Calculated: (a) exact, from ab initio $k(E)$'s; (b) by inversion from eq 1. The two curves were arbitrarily shifted along the concentration axis to bring them into coincidence with each other and with experimental data at $-\log (k_{uni}/k_\infty) = 0.5$. Estimated precision of experimental data: less than about 0.2 log unit in k_{uni}/k_∞.
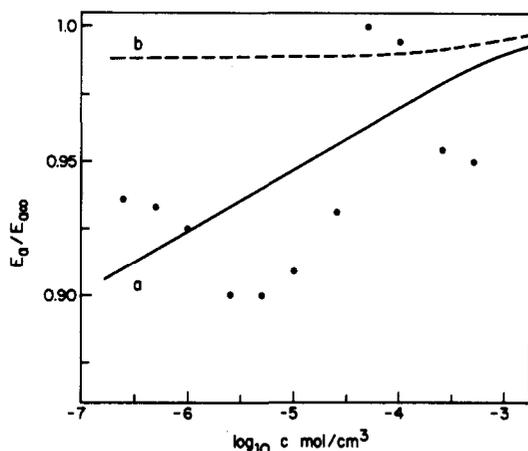

Figure 2. Pressure dependence of activation energy for N_2O decomposition at 888 K. Black dots: composite experimental data as corrected for heterogeneity by Johnston (ref 4, Table III). Calculated: (a) exact, from ab initio $k(E)$'s; (b) by inversion from eq 1. Same shift along concentration axis as in Figure 1. Estimated precision of experimental data: about 0.05 in units of $E_{a\infty}$.

the contribution from a heterogeneous reaction. By interpolation or extrapolation (using observed activation energies), he obtained 31 composite rate constants at 888 K, spanning almost 4 orders of magnitude in concentration. These are shown as black dots in Figure 1. Curve a represents the calculated pressure dependence of exact (calculation a) k_{uni}/k_∞ based on ab initio $k(E)$'s, whereas the dashed curve b represents k_{uni}/k_∞ obtained by inversion of eq 1 (calculation b). Figure 2 shows the pressure dependence of the corresponding activation energies (defined as $E_a = kT^2$ (d ln k_{uni}/dT) and normalized to $E_{a\infty}$).

Although neither calculated curve fits the experimental data at all concentrations, it is clear that, overall, curve a is the more successful representation. This is particularly true of the activation energies, for, despite the great scatter in the experimental data, it is obvious that the activation energies definitely do not obey the trend predicted by curve b.

4. High-Pressure Falloff at 2000 K

At this temperature, the exact calculation (in the sense of calculation a) can no longer be done. The reason is that, when T is high, the influence of the Boltzmann factor

$\exp(-E/kT)$ in the summands of eq 4, 7, and 10 of ref 2 is much reduced, so that very high energy rate constants $k(E)$ start contributing significantly to the summations and therefore have to be computed. Such computations become more and more uncertain as energy increases because, on the one hand, N_2O triplet states higher than the ones considered become important and, on the other hand, Franck–Condon factors for large quantum numbers get progressively less and less accurate due to cumulation of errors in the recursion formula used. Thus, $E \sim 9000$ cm^{-1} above threshold is just about the largest energy at which an exact $k(E)$ can be conveniently computed with good accuracy (ref 1, Figure 2). This energy is large enough for calculations up to about 900 K, but insufficient for calculations at 2000 K.

It is therefore necessary to resort to an expedient in order to extend the energy range of the exact rate constants $k(E)$. We have seen in ref 2 that the Laplace transform inversion procedure reproduces the exact $k(E)$'s quite well if the temperature dependence of $E_{a\infty}$ is known in sufficient detail, either experimentally or from ab initio calculations. In the present instance, the latter is the case below 900 K and the former is the case above 900 K, for it so happens that the cited recommended experimental expression for k_∞ is valid above 900 K and gives the activation energy $E_{a\infty}$ as essentially constant between 900 and 2100 K. Such a constancy is in fact strongly suggested by the ab initio calculated $E_{a\infty}$ shown in Figure 4 of ref 2.

For the purpose of approximating exact $k(E)$'s by inversion over a wider energy range, we combine the ab initio and experimental values of $E_{a\infty}$: thus we take $E_{a\infty}$ at first rising rapidly with temperature and leveling off near 900 K, as given by the ab initio calculation shown in Figure 4 of ref 2, and then take it to be constant at 20 500 cm^{-1} between 900 and 2500 K.

Fitting such $E_{a\infty}$ over the temperature range 150–2500 K according to eq 8 of ref 2 requires, as a minimum, a fifth-degree polynomial in kT, the coefficients of which are as follows: $a_0 = 10482.22$ cm^{-1}, $a_1 = 41.81659$, $a_2 = -0.136287$ (cm^{-1})$^{-1}$, $a_3 = 1.45703 \times 10^{-4}$ (cm^{-1})$^{-2}$, $a_4 = -7.35987 \times 10^8$ (cm^{-1})$^{-3}$, $a_5 = 1.41152 \times 10^{-11}$ (cm^{-1})$^{-4}$, and $C = -315.92389$ s^{-1}. This produces a reasonably satisfactory $E_{a\infty}$ fit, and the $k(E)$ fit below 23 000 cm^{-1} is roughly that of the full line in Figure 1 of ref 2; it produces ultimately rate constants k_{uni} that are good to within a factor of 2 or so. The overall quality of the end result cannot be easily improved upon since increasing the polynomial degree (i.e., improving the $E_{a\infty}$ fit) causes numerical errors in other parts of the calculations to rise also. However, since, in the presentation of the data, k_{uni} is normalized to k_∞, and E_a to $E_{a\infty}$, much of the error disappears because k_{uni}, k_∞ and E_a, $E_{a\infty}$ are affected roughly to the same extent.

Properties based on the fifth-degree polynomial expansion of $E_{a\infty}$ will be referred to, henceforth, as "semiexact" and will be designated as calculation c, whereas calculation b will denote, as before, properties obtained "by inversion" from eq 1, i.e., on the assumption of constant $E_{a\infty}$ at all temperatures, which in turn implies weak energy dependence of $k(E)$.

Figure 3 compares the calculated pressure dependence of k_{uni} for N_2O decomposition in argon with experimental studies of Olschewski, Troe, and Wagner[5] (OTW) and Fishburne and Edse.[6] In both cases the observed rate constant has been divided by 2 on account of secondary reactions, and Fishburne and Edse's k_{uni} normalized to

(5) H. A. Olschewski, J. Troe, and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.*, **70**, 450 (1966).

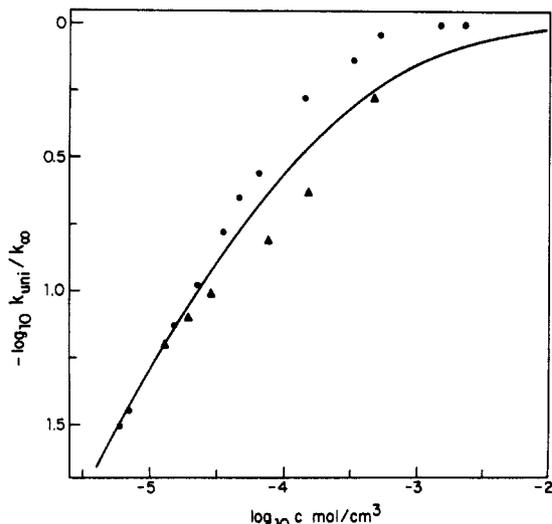(6) E. S. Fishburne and R. Edse, *J. Chem. Phys.*, **41**, 1297 (1964).

Figure 3. Pressure dependence of rate constant from decomposition of N_2O diluted in argon at 2000 K. Experimental: (circles) data of Olschewski, Troe, and Wagner (ref 5, Figure 2); (triangles) data of Fishburne and Edse (ref 6, Table I). After arbitrary shift along pressure axis, both calculation b and c yield the same result (full line). Estimated precision in experimental data as in Figure 1.
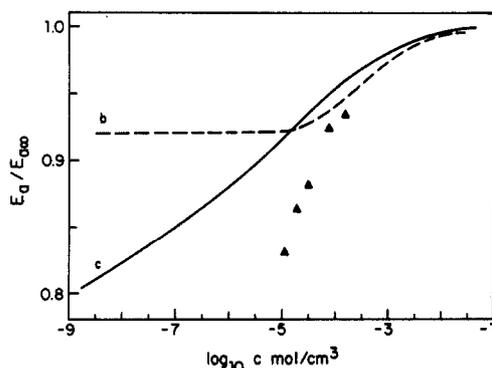

Figure 4. Pressure dependence of activation energy for N_2O decomposition in argon at 2000 K. Experimental: (triangles) data of Fishburne and Edse (ref 6, Table I). Calculated: (b) by inversion; (c) semiexact. Estimated precision of experimental data: about 0.02 in units of $E_{a\infty}$.

OTW's k_∞; the latter actually forms the basis of the cited[3] recommended experimental k_∞. In this case, after the curves are brought into coincidence with each other and with experimental data, both calculations b and c yield the same falloff curve, which fits experiment moderately well.

The situation is quite different, however, if we examine the pressure dependence of activation energy, Figure 4. The two calculations yield a distinctly different pressure dependence, which illustrates the main conclusion of ref 2, namely, that the pressure dependence of activation energy is a much more sensitive indication of the energy dependence of $k(E)$ than the pressure dependence of k_{uni}. It is quite clear that Fishburne and Edse's experimental activation energy does not follow the trend of calculation b, which predicts a leveling off at $E_a/E_{a\infty} = 0.92$, but instead keeps falling off at low pressures as predicted by calculation c, although much more steeply. The considerable steepness may be in part an experimental artifact because it appears that the authors did not allow for self-heating. OTW did not determine the activation energy as a function of pressure, but report $E_a/E_{a\infty} = 0.97$ between 5×10^{-6} and 6×10^{-5} mol/cm^3, which is an even smaller decline than predicted by calculation b. Since calculation b gives the smallest possible decline in activation energy to be expected on theoretical grounds, OTW's results appear to be likewise suspect. (Weak collision effects, not

	limiting low-pressure k_{uni}	k_{uni} at 5×10^{-6} cm^3/mol
$E_a/E_{a\infty}$	0.617	0.960
k_{uni}, cm^3/(mol s)	1.33×10^{12}	8.31×10^9

considered here, would produce an additional decline in activation energy obtained by calculation b).

Comparison of Figures 3 and 4 brings out another important point of ref 2: near-unit slope of log k_{uni} vs. log c plot (this is the case below 10^{-5} mol/cm^3 in Figure 3) is no guarantee that the reaction is actually at the second-order limit, for, as curve c in Figure 4 shows, activation energy is still falling off even at 10^{-9} mol/cm^3.

5. Low-Pressure Limit at 2000 K

There are numerous experimental studies of the N_2O decomposition at the so-called low-pressure limit in the presence of various heat bath gases (for a review see Schofield[7]), but we shall concentrate on the decomposition in argon which is the best studied. Pre-1973 data in argon have been reviewed by Baulch,[3] but newer data in argon are available.[8-11] These studies were generally done at concentrations of $\sim 10^{-5}$ mol/cm^3 or below, where, as Figure 3 shows, log k_{uni}/k_∞ falls off with close to unit slope, which the authors took as evidence that the reaction is at or near the second-order limit, and this is how they interpreted their experimental results. Calculation c, however, shows that near $\sim 10^{-5}$ mol/cm^3 the reaction is still far from the second-order limit (Figure 4).

Since these low-concentration data are (not legitimately, according to calculation c) interpreted in terms of the limiting second-order rate constant, then, for the purpose of facilitating both the comparison with experiment and the calculation of weak-collision effects which become important at low concentrations, we propose to proceed likewise with k_{uni} of calculation c. That is, at a pressure of 5×10^{-6} mol/cm^3, which is near the lower end of the concentrations actually covered in the experiments, we shall first calculate an apparent (strong-collision) limiting low-pressure rate constant k_0 from

$$k_0 = \frac{Z_{LJ}}{Q} \int_{E_0'}^{\infty} N(E)e^{-E/kT} \, dE \qquad (2)$$

but with apparent threshold energy E_0' so adjusted as to give $k_0 = 8.31 \times 10^9$ cm^3/(mol s), which is the (strong-collision) k_{uni} at 5×10^{-6} mol/cm^3 from Table I. It turns out that $E_0' \sim 22700$ cm^{-1} (~ 65 kcal/mol), and this is very close to the value $E_0' \sim 63$-64 kcal/mol deduced in like fashion from experiment and therefore generally assumed[5,12] to be the actual threshold energy E_0 for N_2O decomposition (we have seen that our exact calculation places the threshold energy E_0 much lower at 14135 cm^{-1} (=40.4 kcal/mol), which is also the value used in calculation c).

The weak-collision analog of k_0 can then be calculated from[13]

$$k_0^\dagger = \frac{Z_{LJ} \int_{E_0'}^{\infty} N(E)e^{-E/kT} \, dE}{Q(1 + kT/\gamma)^2} \qquad (3)$$

(7) K. Schofield, *J. Phys. Chem. Ref. Data*, **2**, 25 (1973).
(8) A. M. Dean, *Int. J. Chem. Kinet.*, **8**, 459 (1976).
(9) A. M. Dean and D. C. Steiner, *J. Chem. Phys.*, **66**, 598 (1977).
(10) H. Endo, K Glänzer, and J. Troe, *J. Phys. Chem.*, **83**, 2083 (1979).
(11) I. S. Zaslonko, A. S. Losev, E. V. Mozzhukhin, and Yu. K. Mukoseev, *Kinet. Katal.*, **21**, 311 (1980).
(12) J. Troe, *J. Chem. Phys.*, **66**, 4758 (1977).

TABLE II: Second-Order, Weak-Collision Calculations on the System $N_2O + Ar$ at 5×10^{-6} mol/cm³ Using $E_0' = 22700$ cm⁻¹

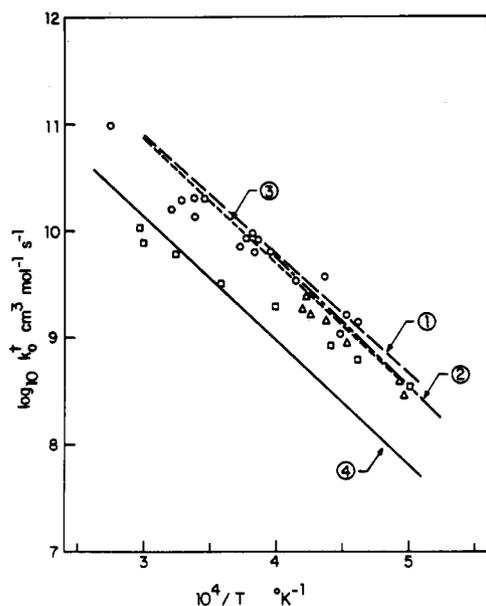| T, K	γ, cm⁻¹	$k_0^\dagger$, cm³/(mol s)	t_{inc}/τ_1
2000	59.5	6.74×10^7	2.65
2500	73.5	1.06×10^9	2.30
3000	80.6	5.31×10^9	2.16

Figure 5. Temperature dependence of second-order rate constant for $N_2O + Ar \rightarrow N_2 + O + Ar$ at 5×10^{-6} mol/cm³. Experimental: (1) ref 8; (2) ref 11; (3) ref 9; (circles) ref 14; (squares) 16; (triangles) ref 5. Calculated: (4) using γ from eq 4.

which requires the knowledge of γ, the average energy lost in a collision. It is calculated from[13]

$$\omega\tau_1 = 1 + \frac{4}{1 + R_1^2}\left[\left(\frac{kT}{\gamma}\right)^2 + \frac{kT}{\gamma}\right] \qquad (4)$$

where the experimentally measured (dimensionless) relaxation time in N_2O–Ar mixtures[14] is used for $\omega\tau_1$, and R_1 is the first solution of[13]

$$\frac{2R}{2 + (\gamma/kT)(1 + R^2)} = \tan\left(\frac{RE_0'}{2kT}\right) \qquad (5)$$

where $E_0' = 22700$ cm⁻¹ is used. Rotational effects are approximately taken into account by calculating $N(E)$ and Q in eq 3 for a system of four oscillators and two rigid rotors. Except for the value of the threshold energy E_0', this part of the calculation in fact proceeds exactly as our earlier calculation on the system[13] in which a slightly different threshold has been used and which may be consulted for details.

The results of the present calculations are shown in Table II, which also includes the ratio of incubation time (t_{inc}) and the relaxation time (τ_1). Comparison with the earlier calculation[13] shows a $k_0^\dagger$ with a somewhat larger activation energy which is to be expected, since threshold E_0' is larger than the previously used E_0, but the other parameters are hardly affected at all, confirming that they are only weak functions of threshold. Curve 4 in Figure 5 compares the present calculated $k_0^\dagger$ with the available

TABLE III: Calculation at 300 K of $k_r = ATe^{-C/kT}$ (C in cm⁻¹) for the Reaction
$O(^3P) + N_2 + M \rightarrow N_2O + M$ (M = N_2O)

	limiting low pressure[a]	10 torr[a]	100 torr[a]	limiting high pressure[b]
A	1.24×10^{-37}	4.65×10^{-41}	1.15×10^{-41}	1.85×10^{-20}
B	0.512	1.512	1.512	0.512
C	251.3	4232.8	4395.3	4491.6
k_r	6.84×10^{-37}	3.95×10^{-46}	4.46×10^{-47}	1.52×10^{-28}

[a] Values of k_r in units of cm⁶/(molecule² s). [b] Values of k_r in units of cm³/(molecule s).

experimental data. It may be seen that the calculated slope (i.e., activation energy) is just about right, but $k_0^\dagger$ is somewhat too small in absolute value (about a factor of 4 at 2000 K). If, instead of obtaining γ from the relaxation time (eq 4), it is calculated from the measured collision efficiency $\beta = k_0^\dagger/k^0$, then[15] $\gamma = \beta^{1/2}kT/(1 - \beta^{1/2})$; at 2000 K, measurement[10] gives $\beta = 0.020$ and hence $\gamma = 231.5$ cm⁻¹, which leads to $k_0^\dagger = 8 \times 10^8$ cm³/(mol s), i.e., about a factor of 3 too high. Thus, while there appears to be some uncertainty about γ, it is quite clear that calculation c leads to no serious disagreement with experiment.

6. Low-Pressure Data at 300 K

At room temperature (300 K), the information of interest is the rate at low pressures of the reverse association

$$N_2 + O(^3P) + M \xrightarrow{k_r} N_2O + M \qquad (6)$$
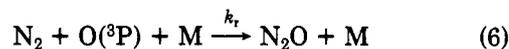
which can be obtained from the forward rate and the equilibrium constant. This forward rate, because of the low temperature, can be obtained by calculation a as the exact rate directly from the ab initio $k(E)$'s. Since the forward reaction is always (according to the calculations) in the falloff regime, it is necessary to specify the pressure. If one takes 10 and 100 torr as the typical pressures for performing the reverse association experiment, calculation a gives for the forward (dissociation) rate constant near 300 K $k_f = 1.318 \times 10^7 \exp(-18151$ cm⁻¹$/kT)$ s⁻¹ at 10 torr and $k_f = 3.25 \times 10^7 \exp(-18314$ cm⁻¹$/kT)$ s⁻¹ at 100 torr. The activation energy is thus a long way from the limiting low-pressure value which we calculate to be $E_{ao} = 13961$ cm⁻¹. From the data of Schofield[7] it can be calculated that the temperature dependence of the equilibrium constant for N_2O dissociation between 300 and 1000 K is given by $K_c = (2.935 \times 10^{27})T^{-0.512} \exp(-13918.5$ cm⁻¹$/kT)$ molecules/cm³, which, combined with the above expressions for k_f, yields the third-order rate constants k_r given in Table III. The table contains for comparison also the limiting (low-pressure) third-order k_r and the limiting (high-pressure) second-order k_r. Considering that the calculations assume strong collisions, the values cited in Table III are upper limits.

An approximate correction for weak-collision and rotational effects can be done in a manner analogous to that shown in section 5, using experimental relaxation times. Around room temperature, these have been measured only in N_2O–N_2O mixtures, the temperature dependence of which in the range 300–700 K can be represented by[17]

$$\omega\tau_1 = 1.24 \exp(58.72/T^{1/3})$$

(13) W. Forst and A. P. Penner, *J. Chem. Phys.*, 72, 1435 (1980).

(14) J. E. Dove, W. S. Nip, and H. Teitelbaum in "15th Symposium (International) on Combustion", The Combustion Institute, Pittsburgh, PA, 1974, p 903.

(15) W. Forst, *Can. J. Chem.*, 59, 2569 (1981).

(16) D. Gutman, R. L. Bedford, A. J. Hay, and R. J. Pancirov, *J. Phys. Chem.*, 70, 1193 (1966).

(17) J. D. Lambert, "Vibrational and Rotational Relaxation in Gases", Clarendon Press, Oxford, 1977, Figure 3.9; *J. Chem. Soc., Faraday Trans.* 2, 68, 364 (1972).

From eq 2 $E_0' \sim 19375$ cm^{-1}, which, when used in eq 4 and 5, gives $\gamma \sim 4.7$ cm^{-1} at 300 K. The weak-collision correction is then $\sim(1 + kT/\gamma)^{-2} = 4.86 \times 10^{-4}$, whereas rotational effects are found to increase the rate by about a factor of 14.4; thus, the combined correction factor is $\sim 7 \times 10^{-3}$, by which the (strong-collision) third-order rate constants in Table III are to be multiplied. Hence, in cm^6/(molecule^2 s), k_r(wc) $\sim 2.8 \times 10^{-48}$ at 10 torr and $\sim 3.12 \times 10^{-49}$ at 100 torr. However, if it should turn out, as in the case of ozone,[15] that relaxation times are an unreliable indicator of γ at low temperatures, we could expect $\gamma \gtrsim 230$ cm^{-1}, in argon, and a combined correction factor of $\gtrsim 3.96$, so that k_r(wc) $\gtrsim 1.6 \times 10^{-45}$ at 10 torr, $\gtrsim 1.8 \times 10^{-46}$ at 100 torr, in the same units.

Such experimental data as are available are only indirect. Extrapolation down to 300 K of k_r recommended by Baulch[3] between 1300 and 2500 K yields $k_r = 3.4 \times 10^{-50}$ cm^6/(molecule^2 s). This is for M = Ar and is advertised as the "second-order limit"; it should be compared with the calculated k_r(wc) at 100 torr, with possibly the allowance that M = Ar should be a less efficient third body than M = N$_2$O. The only direct experimental evidence for the order of magnitude of k_r comes from the work of Stuhl and Niki,[19] who deduced from the *absence* of a contribution of reaction 6 to the decay of (^{3}P) oxygen atoms at 300 K in the presence of N$_2$ pressures up to 345 torr that $k_r \leq 5 \times 10^{-38}$ cm^6/(molecule^2 s).

Thus, the calculated k_r(wc) for 10 and 100 torr at room temperature falls near the low end of what is admittedly a very considerable range of values suggested by experiment.

7. Discussion

If the objective of the present exercise were merely the comparison with experiment of ab initio calculated properties of the N$_2$O decomposition, then the results would have to be termed generally positive in the sense that, on the basis of experimental data available at present, there exists reasonable, and sometimes quite good, agreement between theory and experiment. In order to place the results in proper perspective, is should be mentioned that below 900 K (calculation a) the only datum used in the calculations that is derived from experiment is the value of the spin–orbit coupling constant H^c_{ab}, all of the rest being ab initio. At 2000 K (calculation c) it was necessary to appeal to experiment in order to more definitely confirm the activation energy ($E_{a\infty}$) trend with temperature above 900 K, a trend which theory merely suggests but for the reasons discussed cannot confirm, so that calculation c is no longer entirely ab initio. Also, numerical manipulations get more complex, with concomitant decrease in numerical accuracy; nevertheless, even if calculation c may not be accurate in every detail, it is more than adequate to reveal trends with pressure, which is the principal information of interest for comparison with experiment.

However, if we look for proof positive that the energy dependence of $k(E)$ is indeed the one calculated ab initio, the results are disappointing, because essentially negative: while there is no experimental result that disagrees with what can be calculated from the ab initio $k(E)$'s (calculation a or c), there is also no experimental results that clearly supports it; at best, there is merely a hint.

At 900 K the rate-constant falloff plot in Figure 1 suggests strongly that calculation a gives the better fit with experiment, but the trend with pressure could easily be modified if experimental data were corrected differently

for heterogeneity, so that in this case the shape of the falloff curve is not a foolproof indicator. Similarly, there is strong suggestion in Figure 2 that calculation a gives the better fit of activation energies, but there is too much scatter in the experimental data—probably again because of surface effects—to clearly delineate the pressure trend.

At 2000 K in the shock tube, surface effects are presumably absent, but reduction of the data is not simple. Thus Figure 4, showing the pressure dependence of activation energy $E_{a\infty}$, might constitute the best experimental evidence in favor of calculation c, were it not for the fact that the experimental points[6] shown may not have been properly corrected for secondary effects and are therefore somewhat suspect, whereas the data[5] that presumably were correctly reduced are still suspect for other reasons. At this temperature, rate-constant falloff is quite insensitive to the energy dependence of $k(E)$, as shown in Figure 3, and therefore does not provide a test.

The so-called low-pressure limit does not provide much of a test either. As shown in section 5, experimental data believed to represent the second-order limit can just as successfully be interpreted, on the basis of calculation c, as representing the reaction in the pressure falloff region, and the so-called critical or threshold energy $E_0 \sim 64$ kcal/mol as being merely the activation energy proper to the concentrations at which the experiments were performed, and not the "true" critical energy which we calculate to be at 40.4 kcal/mol.

It is interesting in this connection that there exist what appear to be good low-pressure ($\gtrsim 10^{-5}$ mol/cm^3) shock tube data[7,19-23] which give a low-pressure activation energy of 40.7 kcal/mol (M = Kr) and 43.6 kcal/mol (M = Ne). This cannot be understood at all in terms of calculation b, which predicts a maximum lowering of activation energy only to ~ 56 kcal/mol ($E_a/E_{a\infty} \sim 0.96$), whereas it is understandable in terms of calculation c, which predicts a maximum lowering down to 35.7 kcal/mol ($E_a/E_{a\infty} = 0.62$). However, according to Figure 4 such low activation energies would be reached only at exceedingly low pressures, and it would then be very difficult to explain why $\sim 10^{-5}$ mol/cm^3 of krypton or neon should result in an effective pressure several orders of magnitude less than this. It is to be noted, however, that Fishburne and Edse[6] obtained a low-pressure activation energy of similar magnitude (41.7 kcal/mol) also for M = Ar.

A final point to be considered is the effect of the uncertainty in the spin–orbit coupling constant H^c_{ab}, which means in effect that theory can only produce $k(E)$'s to within a scaling factor. If H^c_{ab} should turn out to be, e.g., 10 times larger ($H^c_{ab} = 105$ cm^{-1}), all rate constants $k(E)$, and also k_∞ and k_{uni}, would increase by 2 orders of magnitude. However, the normalized plots of k_{uni}/k_∞ and of $E_a/E_{a\infty}$ vs. concentration would remain the same, except for a shift of 2 log units to higher concentrations. This would improve absolute pressure fit at 2000 K (i.e., reduce the amount of pressure shift applied), but would worsen it at 888 K, and have no significant effect on the conclusion that the low-pressure limit is unattainable at any practically realizable pressure. Thus, while there would arise a quantitative discrepancy between theory and experiment as to the magnitude of the rate constants, the concentration or pressure trends outlined in this paper would remain

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unaffected. Hence, the exact value of H^c_{ab}, while important, is by no means critical.

8. Summary and Conclusions

Ab initio calculations of the nonadiabatic reaction $N_2O(^1\Sigma) \rightarrow N_2(1\Sigma) + O(^3P)$ show that (i) threshold to reaction is at 14135 cm^{-1} (40.4 kcal/mol), i.e., much lower than generally assumed, (ii) the reaction threshold is not sharp, and (iii) the microcanonical rate constant $k(E)$ is a much stronger function of energy than one would normally expect for a triatomic molecule. In a thermal system, these unusual properties result in (1) a strong temperature-dependent limiting high-pressure activation energy $E_{a\infty}$ at low (<600 K) temperatures, but a constant $E_{a\infty}$ above 900 K, and (2) the general-pressure unimolecular rate constant k_{uni} and the corresponding activation energy E_a remaining pressure dependent (at constant temperature) over an extraordinarily wide range of pressures, such that the low-pressure, second-order limit is in effect beyond reach at any attainable pressure.

While there is no experimental evidence regarding point 1 because of practical difficulties, there are numerous studies regarding the pressure dependence of k_{uni} and of E_a. These experiments in general bear out the ab initio calculations (including calculation c), but in an ambiguous way; that is, either the experiments are suspect for one reason or another, or they do not extend to low enough pressures where the distinction between the ab initio calculations and a more traditional interpretation (calculation b) would be clearer and unmistakable. (However, very low pressures might well be the source of other experimental difficulties.) At the same time, so-called limiting low-pressure, second-order experiments can be satisfactorily interpreted within the framework of the ab initio calculations in terms of k_{uni} in the pressure-dependent region, and the so-called critical energy obtained from these experiments turns out to be merely the pressure-dependent activation energy E_a appropriate to the pressures actually used in the experiments.

The conclusion is, therefore, that available experiments lend a qualified support to the ab initio calculations, in the sense that no experiment clearly contradicts it, and a few experiments seem to give a hint of a more definite support. Obviously more experimental work is needed, preferably direct measurement of the energy dependence of $k(E)$ by one of the newer techniques or, failing that, at least shock tube measurements of activation energy over a wide range of pressures.

Effect of Initial Energy of Hydrogen Atoms on Trapping and Reaction in Solid Methane at 4 K

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The photolysis of HI (or HBr) in the CH$_4$ matrix at 4 K has been studied by ESR spectroscopy. H atoms produced by the photolysis abstract H atoms from CH$_4$ to form CH$_3$ radicals or are trapped in the matrix by losing their energy. In order to obtain H atoms with different kinetic energies, we performed the photolysis with different monochromatic light of 313, 254, 229, and 185 nm. Though the ratio of the yield of CH$_3$ radicals to that of trapped H atoms is almost constant in the kinetic energy range of 0.9–2.4 eV, it increases sharply above 3 eV, which is much higher than the activation energy (0.52 eV) of the H abstraction reaction in the gas phase. The ESR saturation threshold powers of both the trapped H atoms and the CH$_3$ radicals decrease with increase in the initial energy of the H atoms produced by the photolysis. The results indicate that the distances between the trapped H atoms (or CH$_3$ radicals) and the I (or Br) atoms increase with the increase in the initial energy of the H atoms.

Introduction

Hydrogen atoms can be easily trapped in CH$_4$ and are stable for days at 4 K.[1] When hot H atoms are produced by the photolysis of HI or HBr in a CH$_4$ matrix at 4 K, they abstract an H atom from CH$_4$ to form a CH$_3$ radical, or lose their energy, resulting in trapped H atoms (H$_t$). Since both CH$_3$ radical and the H$_t$ atom can be detected by ESR spectroscopy at 4 K, the contributions of the ab-straction reaction and the thermalization of hot H atoms can be estimated directly by measurement of CH$_3$ and H$_t$.

Willard et al.[2] have reported an extensive study on the photolysis of HI at 254 nm and HBr at 185 nm in the CH$_4$ matrix at 5 K. They have obtained two interesting results: (1) The ratio of the yield of CH$_3$ to that of H$_t$ in the 185-nm photolysis of HBr is much higher than the corresponding ratio in the 254-nm photolysis of HI, and (2) the ESR spectra of both H$_t$ and CH$_3$ in a photolyzed CH$_4$–HBr system at 185 nm saturate at much lower microwave power

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