Computational Studies on the Reactions of N_2O with $O(^3P)$ and CO

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We performed *ab initio* molecular orbital calculations to derive rate expressions for the reactions of N_2O with $O(^3P)$ and CO. Major products of the $O(^3P)$ + N_2O reactions are predicted to be NO + NO. Comparisons of calculated and experimental rate constants indicate good agreement exists with the most recent experimental values.

Towards protecting the global atmospheric environment, considerable research attention has been directed at investigating stratospheric chemistry due to potentially harmful substances. The increase of nitrous oxide (N_2O) in the atmosphere impacts the ozone layer in that it and its oxidation products can produce degradation and/or protection effects,[1] as well as N_2O being known to be a greenhouse gas.[2] One important contributor to the global nitrous oxide budget is combustion of fossil fuels,[3] with the production mechanism of N_2O from fluidized bed combustion processes being a recent topic of intense study. One remaining obstacle, however, is that kinetic information on N_2O destruction reactions with $O(^3P)$ and CO remains obscure, i.e., experimental rate constants for the $O(^3P)$ + N_2O and CO + N_2O reactions vary about one or two orders of magnitude. Accordingly, theoretical investigations of the rate constants for these reactions are necessarily important.

In the present letter, we perform *ab initio* molecular orbital calculations using the Gaussian 98 code.[4] All molecular structures, including those for transition states, were determined by using the 6-311G(d,p) basis set and Becke's three-parameter nonlocal exchange functional[5] in conjunction with the nonlocal correlation functional of Lee et al.[6] (B3LYP). With B3LYP/6-311G(d,p) vibrational frequencies in hand, the rate constants were calculated on the basis of a conventional transition-state theory (TST)[7] with the Wigner tunneling correction.[8] Energies of the reactants and the transition states were estimated by the G2[9-11] and G2M(CC1)[12] methodology.

The $O(^3P)$ + N_2O reaction have two product channels that are competitive, i.e., NO + NO (1a) and N_2 + O_2 (1b), and each was found to have two planner transition states with a cis- and trans-configuration. Figure 1 shows their geometries, where TS1 and TS2 are the transition states for (1a), while TS3 and TS4 are those for (1b). Note that all the electronic states of the transition states are $^3A''$. With zero-point energy correction at the G2M(CC1) level of theory, we obtained classical barrier heights relative to reactants for the two competitive channels; namely, 115/138 (TS1/TS2) and 179/254 (TS3/TS4) kJmol^{-1}, respectively. These results clearly indicate the first channel is favorable. There exist the weakly bound dimers of NO in the potential energy surfaces of reaction (1a). It should be noted that the B3LYP underestimated by ca.13% the N-N bond distances[13] of the dimers and the G2M(CC1) energies were above the 2NO asymptote.

TST was used to calculate rate constants for the each channel, after which we compared the resultant overall rate constants k_1 ($k_{1a} + k_{1b}$) and branching ratio of the second channel $k_{1b}/(k_{1a} + k_{1b})$ with experimental results.[14-20] As shown in Figure 2, calculated k_1 values are markedly smaller than those from experiments. Although a similar trend is seen for the branching ratio, good agreement is present with the most recent values obtained by Zuev et al.[20]

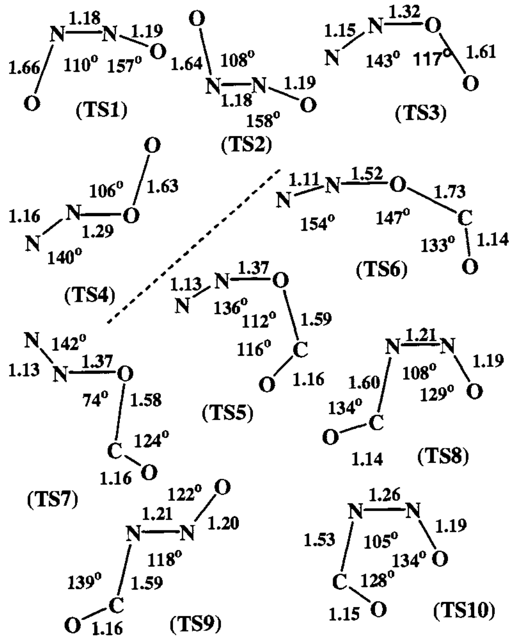

Figure 1. Geometries of transition states for the reactions of N_2O with $O(^3P)$ and CO calculated at the B3LYP/6-311G(d,p) level of theory [all distances in units of 10^{-10} m].

In the N_2O + CO reaction, several product channels exist, e.g., N_2 + CO_2 (2a) and NO + NCO (2b). Two pathways are available for reaction (2a). One is due to the direct exchange of the oxygen atom in which three transition states (TS5-7) are present having potential barriers at the G2 level of theory of 209, 216, and 334 kJmol^{-1}, respectively. The other pathway leads to N_2 + CO_2 and NO + NCO via intermediate singlet OCNNO.

This pathway has been investigated at the HF level of theory by Cooper et al.[21] and at the BAC-MP4 level of theory by Lin et al.,[22] both of whom found that transition states for the addition reaction of CO with N_2O leading to cis- and trans-OCNNO (TS8 and TS9) have the highest potential barriers in the reaction leading to N_2 + CO_2. Accordingly, we reinvestigated the geometry and energy of these transition states in order to compute rate constants for reaction (2a); an effort leading to the discovery of another transition state (TS10) in which both end oxygen atoms in cis-configuration lead to cis-OCNNO. The barrier heights of TS8, TS9, and TS10 were respectively calculated as 199, 297 and 210 kJmol^{-1} at the G2 level of theory, including zero point energy correction. It is noteworthy that the geometry and the potential barriers of TS8 and TS9 show good agreement with those obtained by Lin et al.

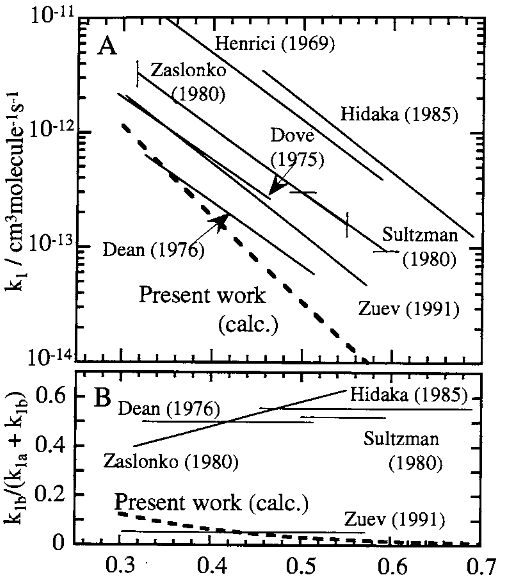

Figure 2. Comparison of calculated and experimental rate constants and branching ratios for the $N_2O + O(^3P)$ reaction.

At the G2 level of theory, the energy of NO + NCO relative to N_2O + CO is 251 $kJmol^{-1}$, which is less than the experimental value of 277 $kJmol^{-1}$, though in good agreement with the theoretical value of 250 $kJmol^{-1}$ obtained alternatively by the theoretical heat of formation of NCO.[23] Reaction (2b) is less favorable product channel because the energy level of NO + NCO is higher than the energy barriers of the product channel (2a).

Using these results in conjunction with TST, we calculated the rate constants k_{2a} for major product channel (2a) and compared values with those from experiments.[24-29] As shown in Figure 3, experimental values show a large discrepancy especially in the magnitude of activation energy, with most values falling into two groups, i.e., about 80 and 200 $kJmol^{-1}$. In comparison, our k_{2a} values are one to two orders of magnitude smaller, although the activation energy show good agreement with those of the latter group.

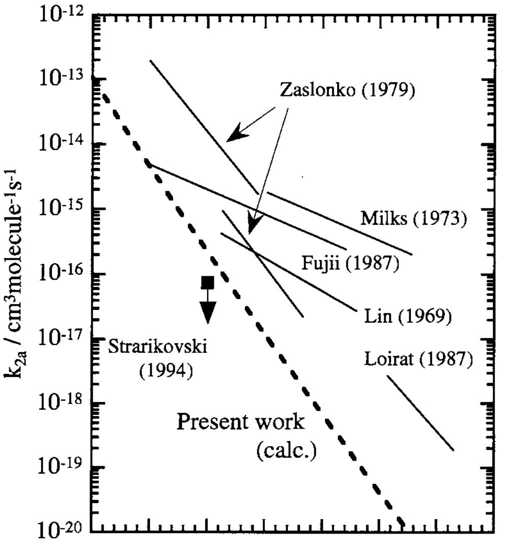

Figure 3. Comparison of calculated and experimental rate constants for the N_2O + CO reaction.

With regard to the most recent experiments by Starikovski,[29] however, k_{2a} at 2000 K was found to have upper limit of 7.5×10^{-17} $cm^3molecule^{-1}s^{-1}$; a value about 70% smaller than that calculated here. While this difference may at first seem large, the results are considered to be consistent when considering that (i) theoretical k_{2a} is expected to have considerable error attributed to the estimation of barrier heights, and (ii) conventional TST rate expressions give an upper limit of the magnitudes. Taken together, these results strongly suggest that the occurrence of another reaction under the conditions of past experiments.

References and Notes

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