Reply to Comment on "Rate Constants for $CH_3 + O_2 \rightarrow CH_3O + O$ at High Temperature and Evidence for $H_2CO + O_2 \rightarrow HCO + HO_2$"

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The reason for this comment is the disagreement in rate constant determinations between work from this group (Yu, Wang, and Frenklach,[1] denoted as YWF) and two recent papers (Michael, Kumaran, and Su,[2] denoted as MKS, and Hwang, Ryu, De Witt, and Rabinowitz,[3] denoted as HRDR) on the reaction, $CH_3 + O_2 \rightarrow CH_3O + O$. HRDR attributed much of the discrepancy of their results with those of YWF to a failure of YWF to apply a boundary layer temperature correction. In their comment,[4] Eiteneer and Frenklach (EF) attribute the differences in both HRDR and MKS results to this issue and raise "the validity of the temperature corrections" that both HRDR and we used. EF support their position by bringing up issues that we believe have already been systematically investigated and discussed previously.

Further, EF suggest that temperature correction procedures may be problematic for other reactions where they also disagree with results from our laboratory. The example given is the reaction $H_2CO + M \rightarrow H + HCO + M$.[5,6] We have compared our H_2CO results to the "boundary layer-less" laser-schlieren results of Kiefer and co-workers[7] and agree within 6 to 17% with them. We have jointly investigated six other thermal dissociations (CCl_4,[8] CF_3Cl,[9] CF_2HCl,[10] $CHCl_3$,[11] CF_3I,[12,13] and CF_3Br[13,14]), in either collaborative or separate studies, and, in all cases, the results agree within combined experimental errors. We are therefore confident that our correction procedures are accurate.

We noted in the MKS study that initial rate analysis (which should be appropriate for the nearly chemical isolation conditions of the work) gave values only ~12% lower than results derived by fitting to an extended mechanism. Allowing that the "temperature correction" effect could explain the discrepancy between YWF and MKS, we have calculated rate constants from the initial slopes assuming that the condition of the gas in the reflected shock wave regime is that from ideal shock wave theory. The resultant rate constants follow the expression $k = 2.56 \times 10^{-11} \exp(-15790\ \mathrm{K}/T)$ cm^3 molecule^{-1} s^{-1}, and this is almost identical to the HRDR expression. Hence, the use of ideal theory only changes our result by 20−30% at most and is still 2 to 2.5 times lower than YWF. We conclude that the disagreement between our and YWF's results cannot be reconciled by differences in considering boundary layer effects.

Regarding shock wave boundary layer theory corrections, Mirels[15] pointed out (reiterated later by Strehlow and Belford[16]) that it is always necessary to characterize a given apparatus. That was the intent of the work of Fujii et al.,[17] Michael and Sutherland (MS),[18] Michael,[19] and HRDR.[3] In bimolecular reaction studies, the approximate reflected shock wave boundary layer theory (i.e., MS) and correction procedures using the adiabatic equation of state were subsequently shown to be accurate in a study[20] not referenced by EF. In this work,[20] the corrected and uncorrected (i.e., ideal) shock tube analyses of results on $O + CH_4$, $H + NH_3$, $O + H_2$, $O + D_2$, $H + D_2$, and $D + H_2$ were compared to low-temperature direct flow tube and flash photolysis-resonance fluorescence (FP-RF) results where the temperature is surely known with higher accuracy than in any shock tube experiment. The general conclusion was that the boundary layer corrected results agreed better with the lower temperature results than the uncorrected results. It is also worth noting that our temperature and density correction procedures have been used in many other bimolecular rate studies from this laboratory. When possible we have continued to compare our results with lower temperature direct chemical kinetics studies in both forward and reverse directions, and these comparisons have always been satisfactory.[21−23] The correction procedures give experimental values[24−26] that also agree with theoretical calculations of rate constants[27,28] on the most fundamental reactions in the field of chemical kinetics (i.e., on $H + D_2$ and $D + H_2$). These calculations use ab initio methods for both potential energy surface and dynamics that are the most fundamental ever performed. This agreement between theory and experiment would be seriously degraded if the thermodynamic state of the hot gas in the reflected regime were calculated using the ideal shock wave description.

In the fifth and sixth paragraphs of the comment, EF review some general points about shock tube apparatus design. We would like to expand this discussion with a few additional observations. Most current shock tube researchers come from the chemical shock tube tradition. In this application, one wants to use the rarefaction wave to quench the reflected shock wave after some well defined dwell time, and it is then necessary to use a driver section that has roughly the same radial dimension as the shock tube itself. For tuning purposes, the axial length of the driver is generally shorter than that of the shock tube. This configuration then ensures that the driving force (i.e., the dynamic pressure) of the driver will not be constant. This immediately means that the incident shock wave will probably attenuate. Also, boundary layer formation causes attenuation, and many workers observe velocities before the flow reaches the limiting condition of Mirels. In either case, the hydrodynamic state (temperature and density) of the gas in the incident wave regime will not be constant as a function of distance behind the shock front. Shock wave reflection into a region of increasing density and temperature has been phenomenologically treated in earlier work;[29,30] however, concurrent boundary layer effects were not considered. It is difficult if not impossible to theoretically model such a system when both effects are contributing. Hence, we can agree with EF that "high-fidelity numerical analysis" might be useful. We note however that the approximate model of MS was quite successful in explaining various hydrodynamic quantities under conditions of a fully developed boundary layer. Therefore, a numerical treatment should be at least as or more successful in explaining the hydrodynamics as the model of MS.

In contrast to the equal diameter driver-driven configuration noted above, the experimental design of the Argonne apparatus has a large driver to driven volume ratio. This is also true of the Brookhaven apparatus. An infinite volume driver tank without walls would ensure a constant dynamic pressure for

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any length of shock tube. We wanted the shock tube to be long enough so that Mirels' limiting plug flow condition could be reached. After that was determined using the MS model (which is only appropriate for limiting conditions), we constructed a driver section tank that had ~3 times the driven section volume. The net result is that our incident shock waves are not attenuated, especially over the last five out of seven velocity gauge intervals. The reason is clear. For any initial thermodynamic condition, Mirels' model predicts that laminar flow follows the shock front until the Reynolds number becomes high enough for turbulence to originate. Using both Mirels' laminar and turbulent theories of boundary layer formation, the position of the contact surface relative to the incident shock front can then be calculated assuming limiting flow (see MS). If this total distance is larger than that of the shock tube then the limiting condition can never be reached. For the loading pressures used in our apparatus, the calculated distance to the contact surface is always less than the total tube length. Hence, the boundary layer is fully developed, and limiting plug flow between the shock front and the contact surface has been reached; i.e., the shock front has slowed and the contact surface has speeded up until both have the same constant velocity. In this case the hydrodynamic state of the incident gas in the laminar region into which the reflected wave will propagate can be determined as a function of distance from the endplate. Then, using the formalism given by MS, the thermodynamic state in the reflected region can be calculated at any distance from the endplate using the laminar boundary layer description. These procedures are all fully explained by MS and Michael,[19] and we always refer to this work in all of our published studies. Therefore, we do not agree with the point made by EF that "not providing such information, like in the case of MKS, creates unnecessary and unproductive 'controversies'." EF have suggested special significance for the measured post-reflected-gas velocities directly observed by Frenklach et al.[31] They point out that these are smaller than those suggested by MS. The reason is probably because their measurements were influenced not only by boundary layer formation but also by attenuation. In any case, considering the approximations used in the MS model, giving quantitative credence to the calculated post-reflected-gas velocities is simply not warranted. In the MS study, the paper by Frenklach et al.[31] was in fact cited as qualitative agreement with the conclusion that minimal flow toward the endplate is to be expected, causing slight adiabatic compression−expansion ripples in the hot gas in the reflected regime.

EF point out that YWF, HRDR, and MKS were all carried out with similar techniques (i.e., "... behind reflected shock waves and the progress of reaction is monitored by optical diagnostics."). For the reasons noted above, it is important to realize that there is no such thing as a generic reflected shock wave apparatus or experiment. Also, the nature of the experiments in the three studies is substantially different. MKS used such high sensitivity for O atom detection that the reaction in question was very close to chemical isolation (i.e., directly measured). On the other hand, the experiments of YWF were carried out with very large initial concentrations and utilized optimization techniques on a very complex reaction scheme, containing, at last count, 325 reversible reactions.[32] Even though optimization is useful in narrowing options as demonstrated by HRDR, a better *modus operandi*, that M (in MKS) and others have advocated for over 35 years, is to build complex mechanisms from well determined direct measurements such as MKS.

EF suggest that nonidealities should be treated as "white noise". We have already made the point that boundary layer temperature and density corrections become comparable to uncertainties in measured shock wave velocities above 1200−1400 K for fully developed flow.[18−21] This of course means that hydrodynamic documentation of the effect is really indeterminate unless one knows velocities with high accuracy. However, nonidealities exist in real shock tubes, and the effects likewise exist, resulting in increasing temperature and density relaxation up from the ideal values. It has therefore always been our opinion[19] that nonideal corrections should be applied to kinetics data because the effect is skewed in one direction toward higher values; i.e., correction is always better than no correction. A detailed discussion of this point is given by Hwang et al.[33] in their accompanying response. Hwang et al.[33] also show that about half of the difference of their results with YWF would have been addressed if YWF had characterized their shock tube and made appropriate nonideal temperature and density corrections.

Peterson and Hanson have recently tested hydrodynamic nonidealities in high-pressure reflected shock wave experiments.[34] In their study, ΔT_5 was directly measured by using CO IR emission, and a theoretical model was used to predict the temperature increase.[29,30] The predicted ΔT_5 values were in excellent agreement with measurements. The main effect was due to attenuation of incident waves. In one case where $T_5 =$ 1450 K and $P_5 = 19.6$ atm, $\Delta T_5 = 38$ K was observed for a dwell time of 500 μs. Using Mirels' laminar and turbulent models for fully developed boundary layers, the calculated distance (~20 m), between the incident shock front and the contact surface, far exceeds the shock tube length at such high pressures. Hence, the limiting distance can never be reached. Therefore, incident waves will always attenuate at high pressures in practical shock tubes necessitating the use of the Rudinger model.[29,30] Even so, we have calculated the expected temperature increase at 2 cm from the endplate using the fully developed MS laminar model. Since the limiting condition is not close to being attained, the calculated value will be overestimated. The calculation gives $\Delta T_5 = 6$ K for the experiment noted above; i.e., boundary layer formation is not nearly as important as attenuation. The point to this illustration is to reinforce the idea that all shock tubes should be characterized for the conditions under which they are to be used as done, in incident waves by Strehlow and Cohen,[35] Skinner et al.,[36] Belles and Brabbs,[37] Bertin et al.,[38] and Fujii et al.,[17] and in reflected waves by MS,[18] Michael,[19] HRDR,[3] and, now, Peterson and Hanson.[34]

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