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Reply to the Comment on "Rate Coefficient Measurements of the Reaction $CH_3 + O_2 = CH_3O + O$"

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In their comment Eiteneer and Frenklach[1] (EF) raise a series of technical and philosophical objections to the results of two recent studies that disagree with the rate coefficients for the reaction $CH_3 + O_2 = CH_3O + O$ previously reported by their group (Yu et al.,[2] YWF). They claim that the results of Michael et al.[3] (MKS) and Hwang et al.[4] (HRDR; referred to as HRWR by EF) are in error due to a correction that MKS and HRDR apply to their measured temperatures. This correction is used to account for boundary layer effects that result in an upward shift from the temperatures calculated using ideal shock theory. The validity of this correction is also addressed in an accompanying reply by Michael.[5] We first wish to address the issue at the heart of EF's comment, namely the apparent agreement between the characteristic times, t_{ABS50}, measured by YWF and HRDR for the one mixture common to both studies.

As shown in Figure 5 of HRDR the t_{ABS50} values measured by HRDR are always longer than those measured by YWF. Moreover, the HRDR experiments were performed at higher densities where shorter t_{ABS50} values would have been expected. Those longer t_{ABS50} values resulted in rate coefficient expressions that are $^1/_3$ the YWF value based on the corrected temperatures and $^2/_3$ the YWF based on the uncorrected temperatures. Thus, the temperature correction represents the bulk but not the basis of the difference.

EF express concern that MKS and HRDR may be promoting controversy and deviating from "majority practice" by their use of corrected temperatures. It is a truism that yesterday's controversies are today's orthodoxies; the title reaction is an abiding example. The assignment of a nonzero rate to the title reaction was quite controversial in 1974 when Brabbs and Brokaw[6] first parted ways with majority practice and proposed it as the only way to explain their data. After some initial reluctance majority practice has come to accept a nonzero value for the rate of the title reaction. Indeed, we are here arguing about that value. Various groups may obtain different results depending upon the suitability of their experimental and analytical techniques for the particular system under study. Greatest credence is accorded to the results of those groups that achieve agreement using different experimental conditions. For the title reaction this is the case for three of the four most recent determinations. At 1600 K the rate coefficients of Braun-Unkhoff et al.[7] (BNF; not mentioned by EF), HRDR and MKS yield a narrow range of values, BNF being 25% higher than HRDR who are, in turn, 24% higher than MKS. YWF's rate coefficient is a factor of 2 higher than BNF. It is pertinent that HRDR agree with the two experiments (BNF and MKS) performed with dilute mixtures where secondary reactions are perforce less important. Obviously, when the total rate of reaction is fixed by careful measurement the rate of the primary reaction must be reduced when secondary pathways are active; these secondary pathways are active for the conditions used by YWF and HRDR. The belief that secondary chemistry was responsible for the wide range of rate coefficients reported for the title reaction was the stated motivation of the HRDR study.

EF assert that the current well developed understanding of shock−boundary layer interactions is insufficient for the task of determining the magnitude, or even sign, of a temperature correction. This argument is coupled to a misreading of the work of Werner et al.[8] (WTHR) where the stated objective was the study of boundary layer effects upon ignition characteristics measured in strong air-like methane mixtures. The shock−boundary layer interaction grows with both mixture strength and increasing distance from the end wall, and so WTHR purposefully chose these conditions. The mixtures and conditions that they used are representative of those used in practical applications such as aerospace propulsion and ground power generation. For the same reason similar mixtures were chosen as optimization targets in the development of the GRI_MECH2.11[9] and GRI_MECH3.0[10] mechanisms. That the viscous boundary layer and its time history affect the thermodynamic state of the gas behind both incident and reflected shock waves is well-known. Indeed, EF claim both that "YWF chose to minimize this effect by diluting the mixture" and that YWF corrected their temperature for shock attenuation (caused by viscous boundary layer development).

Theoretical analysis and experimental studies of the boundary layer effects have been actively pursued for nearly 50 years. Seminal studies were performed by Mirels[11] (incident shocks) and Mark[12] (reflected shocks). Mark observed shock bifurcation due to reflected shock−boundary layer interaction in an extensive series of experiments using schlieren photographs of the flow. Numerous other investigators[13−23] confirmed his findings using optical techniques and side wall pressure measurements. These efforts have led to a durable understanding of the phenomena involved. Theory predicts, and experiment confirms, that when the stagnation pressure in the boundary layer is below the reflected shock pressure the boundary layer is "rolled up" and a shock bifurcation forms. Center[16] and Sanderson[17] observed the signature of the bifurcation as an abrupt change in the slope of the pressure rise and, as the bifurcation grows with increasing displacement from the end wall, eventually a stepped appearance. Excellent examples of this signature observed in methane ignition experiments have been reported by Petersen et al.[24] (their Figure 2) and WTHR (their Figure 1). The necessary conditions for shock bifurcation are those typical of chemical kinetics experiments. For pure Ar ($\gamma = 1.67$) this condition exists for Mach numbers between 1.5 and 3 and, increasing rapidly with decreasing γ, extending to 6 for air ($\gamma = 1.40$). Shock Mach numbers near 2.75 were used by both YWF and HRDR for the 0.5% CH_4/10.0% O_2/ 89.5% Ar mixture ($\gamma = 1.62$) common to both studies. Thus, the temperature measurements of YWF and HRDR were both affected by reflected shock−boundary layer interactions.

We agree with EF that important work remains uncompleted in boundary layer theory, especially in the area of laminar-to-

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turbulent transition. We also agree that a comprehensive high-fidelity numerical simulation of reflected shock−boundary layer interaction would be informative. Nevertheless, easily applicable methodologies, based upon sound theoretical underpinnings, are currently available for determining the magnitude of the effect using actual and proxy measurements of the thermodynamic state of the gas behind shock waves. Therefore, we disagree with the assertion of EF that we must await complete theoretical development before any temperature correction may be applied.

EF criticize the adiabatic equation of state (AES) methodology for being “simplistic”. This methodology is based on well established boundary layer theory. The AES correctly describes the change in thermodynamic state of a gas undergoing an adiabatic compression or expansion. This is the case for the gas behind a reflected shock−boundary layer bifurcation. The extensive validation of the AES approach performed by Michael and co-workers is discussed in the accompanying response. Unlike Michael we measure the pressure for each experiment and do not rely upon empirical relationships. This is not due to a flaw in the Michael’s procedure but rather to a difference in operating conditions. We employ a wide range of preshock pressures, mixture compositions and mixture strengths to study conditions representative of aerospace propulsion systems. The AES methodology is reliable, accurate and simple, and not, “simplistic”.

EF argue that the correction is itself small and so should be treated as white noise. The correction measured by HRDR is, however, not small, being 24 K (1.4%) on average. This represents a shift that is nearly 5 times larger than the 4 K (0.3%) uncertainty bound in HRDR’s ideal temperature determination. EF also argue that the temperature correction is small based on their Figure 1, which shows the residuals obtained by systematically changing the temperature correction applied to the WTHR 9.1% CH_4/18.2% O_2/72.7% Ar mixture ignition delay data. The reduction in residuals is about a factor of 3 at 50% of the correction and about a factor of 4 at 100%. (The rise in residuals above 100%, not shown, mirrors the reduction.) While this might be taken as evidence in favor of the temperature correction, EF argue that the difference between the 50% and 100% residual reduction is insignificant and so the actual correction is at most 50% of the WTHR correction; a value that is equal to the upper end of the YWF temperature uncertainty. EF therefore argue that the actual corrected temperature falls within the uncertainty of the uncorrected temperature, and so, it is no different than the random experimental artifacts that contribute to that uncertainty. Thus, EF transform a shift in the mean of a distribution into an increase in the width of that distribution. As support for their transformation EF invoke the central limit theorem[25,26] (CLT). Normally the CLT is used to explain why a series of unique measurements with different means and arbitrary uncertainty distributions, when summed, result in a normal uncertainty distribution and a new mean. To do so the CLT requires a sufficient number of measurements whose means are not unduly separated. If we were to treat the ideal and corrected temperatures as unique measurements and assume that they met this criterion (which they do not because their uncertainties are small compared to their separation) we could then sum them and determine new mean temperatures. Using these mean temperatures and the HRDR characteristic times yields rate coefficients that are about $^1/_2$ those of YWF.

EF further argue that the necessity and validity of the temperature correction were tested and found wanting in an “extensive” series of experiments performed by Bott and Cohen (BC83[27] and BC91[28]). Actually, the BC83 data analysis depends critically upon the temperature rise due to incident shock−boundary layer growth. BC83 used a 1% DF in Ar mixture to study the rate of DF thermal dissociation for their incident shock experiments. For a 30% dissociation (the BC83 observation period) they calculate that the reaction endothermicity would have lowered the gas temperature by 1.2% (the D−F bond is very strong). That drop in temperature would result in a decrease in the apparent rate that BC83 should have observed; instead they observed that the apparent rate tended to increase as the temperature decreased. BC83 posited that the gas was heated as a result of boundary layer growth and that the resultant temperature increase, 0.6%, would have somewhat counterbalanced the cooling. BC83 went on to argue that the “average” temperature during their observation period would then have been 0.3% lower than their ideal temperature, a tolerable and “small” displacement that would have resulted in a 4% shift in the rate coefficient. (For the experimental condition of YWF and HRDR, without the offsetting reaction endothermicity, the temperature correction is nearly 5 times greater.) BC83 proposed that for their lower temperatures the increase in apparent rate may have been due to laminar-to-turbulent transition in the boundary layer resulting in an increased temperature rise for those experiments. BC83 assumed that this transition would have occurred when the boundary layer Reynolds number rose to 2×10^6 but that it may have occurred earlier. Bander and Sanzone[29] correlated laminar-to-turbulent transition times for incident boundary layer experiments and determined that the transition takes place one tube diameter behind the shock front. For the BC83 shock velocities this would imply that all but their highest temperature data would have experienced enhanced boundary layer heating.

In BC91 all the experiments were performed behind reflected shock waves. As part of their overall study BC91 measured the long-term pressure behavior to see if it rose in accord with the boundary layer correction of Michael and Sutherland[30] (MS). BC91 used an unshielded Kistler pressure transducer. It is well-known that boundary layer heat transfer to the front face of such a transducer causes spuriously low pressure readings. This problem has been addressed most recently by Petersen and Hanson[31] (PH) and can be seen clearly in their Figure 4 where the pressure rise measured using shielded and unshielded transducers is shown. Figure 3 of PH shows the long-term pressure rise behind reflected shocks that is easily measured using shielded pressure transducers. This effect undoubtedly misled Skinner[32] who also used an unshielded Kistler gauge in his experiments and reported that there was a 30−50 K drop in temperature due to boundary layer effects. He reversed his position in a later paper[33] where he studied the well characterized decomposition of cyclohexene that required a 50−60 K increase above the ideal temperature to explain his observations. Unsurprisingly, BC91 saw no pressure rise using their unshielded pressure. Thus, BC83 and BC91 represent neither an extensive nor a negative test of the temperature correction.

EF’s final argument is that transient pressure measurements can have 10% noise and so are unsuitable for measurements on the 1−2% level. For the side wall mounted transducers used by HRDR and PH the noise level is less than 1%. We further reduce the impact of noise by averaging the first 20 μs of signal. This represents 10 cycles of resonant frequency for our transducer. It is true that end wall mounted pressure transducers do experience greater noise due to the greater impulse of receiving a shock wave traveling normal to the transducer face. This fact is, however, not relevant to measurements made using side wall mounted transducers.

EF end their comment with a suggestion for improving the state of kinetics research. We agree that a meta-analysis, such as that undertaken by the GRI_MECH consortium, can result in an improved "overall" reaction mechanism, and certainly one more useful for a specific application. It should be noted that one of us (MJR) is an author of the paper[34] that the GRI_MECH consortium references as the basis for their approach.[10] Nevertheless, that approach was not meant to be a substitute for improvements in the determination of the rate coefficients of the individual reactions. The approach was meant, and is useful, as a method of understanding the effects of unavoidable secondary reaction chemistry on individual rate coefficient measurements. We agree with Michael that improvement in the accuracy and applicability of detailed chemical mechanisms is best achieved by reducing the uncertainty in individual rate coefficient measurements. We maintain that correcting the ideal temperature for well-known boundary layer effects is necessary for realizing that goal.

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