COMMENTS

Comment on "Rate Constants for $CH_3 + O_2 \rightarrow CH_3O + O$ at High Temperature and Evidence for $H_2CO + O_2 \rightarrow HCO + HO_2$" and "Rate Coefficient Measurements of the Reaction $CH_3 + O_2 = CH_3O + O$"

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Shock tubes have developed into a dependable experimental technique for high-temperature chemical kinetics. The measurements, however, are not without uncertainties and extreme care must be exercised at every step of data reduction. With the demand for higher accuracy reaction kinetics, where a factor of 2 uncertainty in rate coefficient is of concern, finer and finer details must enter the data analysis.

The subject of present communication is reaction $CH_3 + O_2 \rightarrow CH_3O + O$. Oxidation of methyl is one of the pivotal constituents of detailed combustion models and hence its mechanism and kinetics have been under repeated investigation and surrounded with controversies over the past several decades (for references see citations below). Recent reports[1,2] have refueled the controversy. While resolving this individual case is of interest in its own right, the present analysis has implications to other reaction systems, to shock-tube measurements in general, and, ultimately, to development of detailed kinetic models.

Michael et al.[1] (MKS) and Hwang et al.[2] (HRWR) reinvestigated methyl oxidation, both studies carried out behind reflected shock waves, within overlapping temperature ranges, but at different initial mixture compositions and pressures, and using different optical detection techniques. The two groups reached opposite conclusions over existence of the secondary channel ($CH_3 + O_2 \rightarrow CH_2O + OH$) but reported a close agreement on the rate coefficient determined for the primary channel, the subject reaction of the present discussion. The problem appears as the MKS and HRWR values are about a factor of 3 lower than the previous determination by Yu et al.[3] (YWF).

Possible sources of the disagreement were thoroughly investigated by HRWR. First, they performed a series of experiments at conditions matching those of YWF and found the measurements in agreement with each other, thus ruling out an "experimental error". Then HRWR looked at the differences in the thermochemical assignments used in data analysis and found them to account for no more than 17% reduction in the rate coefficient. The main factor was identified to be the temperature correction for nonideal shock-wave behavior applied by HRWR and MKS but not YWF. It is very likely that the disagreement between another set of rate coefficients,[4,5] for reaction $CH_2O + M \rightarrow H + HCO + M$, is due to the same factor. The issue therefore is the validity of the temperature correction.

A shock-tube apparatus is a tube with smooth internal walls separated by a breakable diaphragm between the reacting mixture and pressurized driver gas. Upon bursting of the diaphragm, a shock wave is created which propagates through the reacting gas, leaving it compressed, heated and moving. The shock wave is reflected at the end plate of the tube, compressing and heating the reacting gas further. The three studies—YWF, MKS, and HRWR—employed one of the common modes of shock-tube operation in which the initial conditions are chosen so that the reaction is initiated behind reflected shock waves and the progress of reaction is monitored by optical diagnostics.

One of the principal sources of experimental uncertainty is rooted in the determination of reaction temperature. Its value is obtained by solving the mass, momentum, and energy conservation equations with the measured incident shock-front velocity as an input. Efforts are made to minimize departure from idealized assumptions, like ideal-gas equation of state and one-dimensional flow. Still, many problems remain: imperfect bursting of the diaphragm, wall roughness, development of a boundary layer, shock-front curvature, and so forth. As a result, the incident shock-front velocity attenuates, typically 0.5 to 3% per meter, which translates to about 10−30 K "correction" in the reaction temperature. This correction was applied in data reduction by HRWR and YWF; MKS reported no velocity attenuation.

The central issue of the present discussion is the further correction to reaction temperature suggested[6] to account for the boundary layer interaction with the reflected shock wave. This is a complex phenomenon which has neither complete experimental documentation nor accurate theoretical treatment. A very simplified treatment, with the use of the isentropic-process relationship, was applied by MKS and HRWR to modify the reaction temperature, and it is this correction which was identified by HRWR to be largely responsible for their lower rate coefficient as compared to that of YWF.

The use of the isentropic-process approximation in shock-tube data analysis originates probably with Mirels[7] who invoked it for a simplified laminar-boundary-layer theory of incident shock waves. Skinner et al.[8,9] adopted this approximation to correct for a marked expansion/compression of the reacting gas behind reflected shock waves. Michael and Sutherland[6] (MS) justified the validity of this treatment on the basis of agreement with predictions of Mirels' theory.[7,10] The agreement is indeed satisfactory as far as qualitative trends are concerned, but in quantitative terms the discrepancy in the reflected-shock temperature is within 1 to 2%, depending on shock-tube characteristics and experimental conditions.[6,11] The above quoted percentage translates into 10−20 and 20−40 K for a reaction temperature of 1000 and 2000 K, respectively, that is, comparable in magnitude to the uncertainty due to other nonidealities associated with shock-tube operation. In fact, in a follow-up study, Michael[12] concluded that for tube diameters above 6 cm and reflected shock temperatures above 1200−1400 K "the correction becomes comparable to uncertainties caused by shock velocity measuring errors."

The MS correction procedure did not receive wide acceptance. The reason for this can be exemplified by the conclusions of Bott and Cohen[13,14] who performed an extensive series of shock-tube experiments in both incident and reflected shock regimes.

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These authors reported the temperature correction following MS below 10 K and simply included this estimate into the compound uncertainty of temperature measurement.

Unfortunately, it is rather difficult, if not impossible, to quantify the accuracy of the simplified theory for the boundary layer interaction. A rigorous computational treatment is not yet possible even for the laminar flow of a reacting gas, and one actually expects the development of a turbulent boundary layer behind reflected shock waves.[6,7,15,16] Experimentally, reflected shock velocity is universally found to be of little assistance to narrowing down the uncertainty in temperature, and the pressure traces, required for the isentropic-process relationship, are typically too noisy. For instance, a 1% error in reflected-shock pressure translates into a 0.4% error in reflected-shock temperature, whereas pressure "oscillations" of up to 10% are not unusual. That is, the uncertainty of the pressure-based correction is of the same order of magnitude as the correction itself.

There is one instance where Mirels' theory can be tested with a higher "resolution". According to the idealized one-dimensional solution, the gas behind the reflected shock front comes to a halt. Mirels' laminar-boundary-layer theory[6,7,10] makes definite predictions for the velocity of the gas, and such gas motion was observed experimentally.[17] In the latter study, the post-reflected-shock gas velocities were measured directly, by laser Doppler velocimetry. The experiments were performed in a 7.62 cm inner-diameter shock tube using Al_2O_3 seed particles in argon, nitrogen, and hydrogen−oxygen mixtures, as well as nascent soot particles in argon−toluene mixtures. In pure argon at reflected-shock conditions $T_5 = 1864$ K and $P_5 = 2.07$ atm the gas velocity measured on the centerline of the shock tube, 1 cm from the end plate was 0.56 m/s, effectively zero considering the experimental scatter. Application, following MS, of Mirels' laminar-boundary-layer theory gives a value of −5.4 m/s for this case, where the negative sign indicates flow in opposite direction from the reflected shock. For $T_5 = 1670$ K and $P_5 = 1.76$ atm the centerline gas velocity, measured 8.5 cm from the end plate, was −3.23 m/s, whereas the theory predicts −15.1 m/s. The corresponding MS temperature correction for the latter case is 38 K. As an order-of-magnitude sensitivity test, matching the experimental velocity by adjusting the reflected shock Mach number of the theory reduces the temperature correction from 38 to 9.5 K. This demonstrates that applying the MS correction may greatly overestimate the magnitude of temperature variation.

In support of this conclusion, let us consider an earlier report, that of Werner et al.,[18] who measured ignition delays in methane−oxygen−argon mixtures at several locations of the shock tube. As expected,[19] the ignition delays decrease as the measurement station moves away from the end plate of the shock tube. Werner et al. noticed that all the measured data collapse into a single Arrhenius-like line when the reaction temperature is adjusted following, and seemingly validating, the MS treatment. However, essentially the same quality of fit can be obtained if the original temperatures[18] are changed just by one-half of the MS correction, as can be witnessed from Figure 1 which depicts the least-squares residuals as a function of the multiplier to the MS temperature correction. (It is pertinent to mention, though, that the sizable dependence of the ignition delays on the probe location is due to a relatively high "strength" of the mixture[18]—9.1% CH_4 and 18.2% O_2. YWF chose to minimize this effect by diluting the mixture.)

Thus, while the development of a boundary layer undoubtedly impacts the interpretation of shock-tube measurements, the available data do not necessarily support the correction at the extent suggested by MS and applied in MKS and HRWR studies. For a replicating set of experiments, HRWR reported that the difference in the rate coefficient determination for reaction $CH_3 + O_2 \rightarrow CH_3O + O$ is essentially due to the 24 K MS-correction they applied to the reaction temperature. On the basis of the analysis presented above, this correction should be at least twice smaller, on the order of 10 K, which makes it comparable in magnitude to the uncertainties associated with other nonidealities of shock-tube operation.

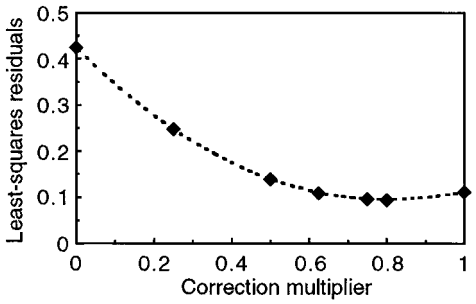

Figure 1. Least-squares residuals of the induction times[18] versus a multiplier to the MS temperature correction.

Should this correction be applied at all? Majority practice, including our own, is not to treat it as a systematic correction. Instead, efforts are being made to minimize nonidealities of shock-tube operation—by using sufficiently large diameter tubes, with smooth internal walls, observation stations positioned close to the end plate, not too low initial pressure, and so forth—and to consider boundary-layer interactions as one of the factors contributing to the compound uncertainty of shock-tube measurements. The latter view is consistent with the very nature of random errors specified by the central limit theorem which asserts[20] that the overall error caused by many fairly small, equally contributing factors will tend to normal distribution, i.e., to "white noise". Nonetheless, whenever the boundary-layer correction is applied and is shown to cause a significant difference, the details must be documented at a level sufficient to recover the original data.

Finally, in light of such uncertainties, what can or should be done for the development of predictive reaction models—currently the primary motivation for the experimental shock-tube kinetics? Obviously, one has to strive for accurate measurements. In this regard, it would be revealing to undertake a high-fidelity numerical analysis of the boundary-layer development in shock-induced reactive flows. Such an undertaking is a good scientific and numerical challenge even at the present level of computer technology. Still, having done this, the result may be that to correct the measurement would require extensive and sophisticated instrumentation (e.g., to probe the gas velocity field) thereby introducing additional uncertainties or making the approach impractical. In other words, we may have no choice but to accept this level of experimental uncertainty as given, quantify its implications, and recover information by using theory and complementing experiment data. One such approach,[21] through a systematic model building and error analysis, has been successfully applied[22] to natural gas combustion.

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