Measuring Temperature of Reflected Shock Wave Using a Standard Chemical Reaction

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Abstract | The importance of temperature calibration of a single pulse shock tube for obtaining precise kinetics data is well recognized. Some of the commonly used standard reactions for chemical thermometric measurements and their uses in our recent studies are discussed in this article. The chemical standards listed include cyclopropane-carbonitrile, 1,1,1-trifluoroethane, cyclohexene, and ethyl chloride. A recent temperature calibration study of one of our chemical shock tubes performed using ethyl chloride as external standard for the temperature range from 982–1183 K is presented. The reflected shock temperatures calculated using mach number, $T_{5(Ms)}$, and those using ethyl chloride as external standard (T_{5kin}) were found to differ by ~1.3–4.5 % in the studied temperature range. This is an improvement compared to our previously reported calibration data where the corresponding difference was in the range ~8–14 %. The difference in the calibration factor is due to the various changes made in the shock tube and it highlights the importance of calibration, if and when the shock tube is modified.

Keywords: *Single pulse shock tube; Chemical kinetics; Chemical thermometry; Gas Chromatography*

1 Introduction

Shock tube is a device generally known for its ability to generate high temperature and pressure for a short duration ranging from a few microseconds to a few milliseconds. Hence, it is also considered to be a millisecond high temperature furnace.[1] Kineticists all over the world use the shock tube as a high temperature wave reactor for obtaining rate coefficient data under diffusion free conditions as it provides a nearly one-dimensional flow, with practically instantaneous heating of reactants.[2] The temperature range under which the reaction could be studied can be extended far beyond that of the conventional flow reactor (1000 K). The device has also been extensively used for various applications including hypersonic research, geosciences, condensed matter physics, material synthesis (initiated using shock wave) and in the field of medical and biological applications.[3,4] In this article, calibration of a shock tube using chemical standards is discussed. We begin with a brief discussion of the principles of shock tube operation for the benefit of general readers.

2 Single Pulse Shock Tube

A shock tube in its simplest form is basically a long cylindrical tube with closed ends separated into two sections by a diaphragm.[3] The test gas mixture is placed in the driven (low-pressure, P_1) section of the tube and the driver section of the tube is filled to high pressure with a low molecular weight gas. It is often helium. While H_2 with a lower mass could be better than He, it is avoided because of the danger involved in handling it. On pressurizing the driver section (P_4), the diaphragm suddenly ruptures resulting in creation of a planar shock wave. This shock wave moves rapidly ahead of the driver gas expanding into the driven section and compressing the gases in the driven section. Distance between the shock front, i.e. primary shock wave and the driver gas following it, increases as the shock front moves with supersonic

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speed. When the diaphragm ruptures, another rarefaction wave (also referred to as expansion fan) travels in the opposite direction through the driven section. The test gas and the driver gas make contact at the 'contact surface', which moves along the tube behind the shock front. The primary shock wave gets reflected at the end of the driven section and rams into the shocked gas flowing behind it, thereby causing further rise in temperature (T_5) and pressure (P_5) of the test gas.[2] The expansion fan also gets reflected form the end flange of the driver section and travels back into the driven section, and reaches the reflected shock in the contact zone. These physical phenomena are shown in Figure 1, and are commonly kn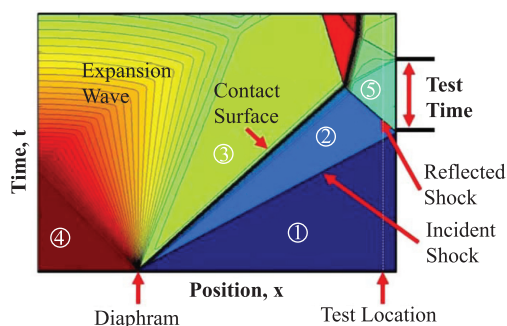own as the x-t diagram where x represents the distance along the shock tube and t, given in y axis represents the time. The propagation of the primary shock can be seen from the diaphragm towards right and the expansion fan towards left.

With proper choice of the driver and driven gases along with proper adjustments of the driver and driven section lengths, the expansion fan can be directed to meet the reflected shock wave before it meets the contact surface. When the reflected shock meets the contact surface, it can be reflected either as a shock or expansion wave leading to change in T and P that will affect chemical reactions. If the expansion fan meets the reflected shock before it hits the contact surface, it will quench the heated gas and all activated reactions would be stopped. In this way uniform temperature and pressure (i.e. uniform T_5 and P_5) can be achieved. The time duration, in which the reflected shock wave survives before it is quenched due to the arrival of expansion fan, is the reaction time and is known as dwell time. This complete operation takes place in few milliseconds. Using the reflected wave for heating and expansion fan for cooling in this manner is known as single pulse operation (hence is called a single pulse shock tube, SPST). The single pulse shock tube built in our laboratory, called CST-1, uses such conditions for kinetic studies.[5,6] A schematic of our shock tube is shown in Figure 2 and the x-t diagram shown in Figure 3 shows the primary and reflected shock waves and the arrival of expansion fan.

The dwell time in our shock tube is typically about 1 ms. With advances in shock tube research, shock tubes capable of producing test times up to 100 ms have been recently demonstrated.[7] Thus

Figure 1: The x-t diagram of shock/expansion wave propagation in a typical shock tube. The reflected shock raises the temperature and pressure (see Figure 4) of the test molecules for the duration of test time. (Reprinted from Ref. 11 with permission from Elsevier).
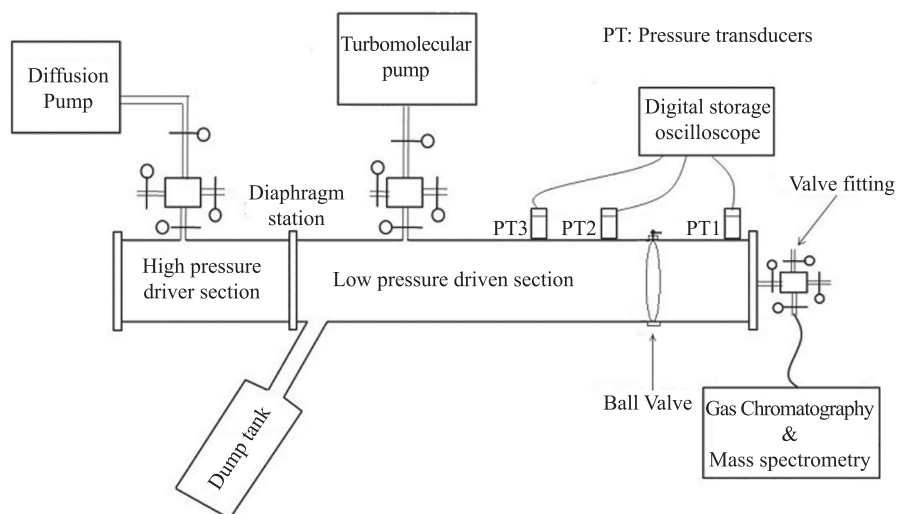

Figure 2: Schematic of the single pulse shock tube, CST-1, at the Indian Institute of Science. The ball valve is crucial to ensure that all the test molecules are heated by the reflected shock wave. See Figure 5.
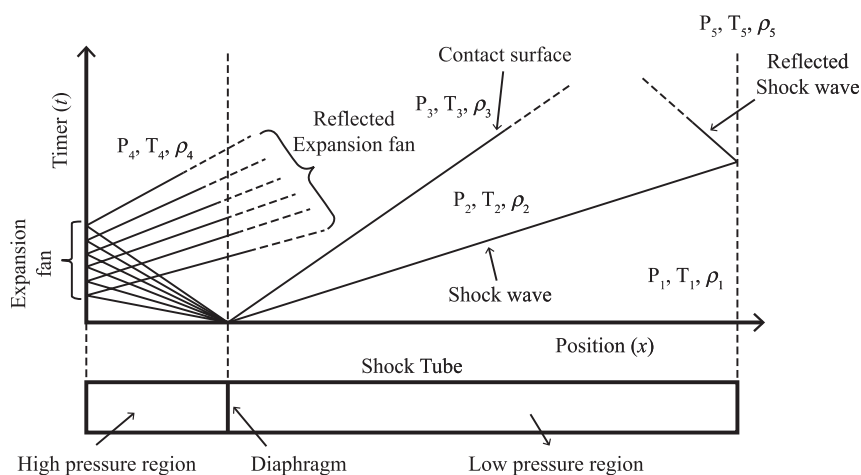
Figure 3: The x-t diagram of shock/expansion wave propagation applicable for the shock tube shown in Figure 2. The expansion fan meets the reflected wave before it reaches the contact surface. See discussion.

the test gas under study is exposed to only the reflected shock temperature (but not the ramp i.e. from the room temperature to the reflected shock temperature). The single pulse mode of operation is easily achieved by incorporating an evacuated dump chamber[8,9] (called dump tank) near to the diaphragm station in the driven section at an angle of 45° to shock tube. The dump tank serves the purpose of quenching the multiple reflections which can lead to shock waves of smaller intensity. According to Bauer and Lifshitz,[9] the main reasons of using a dump tank is to 'swallow' the cold driver gas that was not heated in the shock, thereby quenching reflection in the reflected shock region (zone 5) in order to obtain very well defined reaction time and uniform temperature during the reaction time. A pressure trace from a typical experiment is shown in Figure 4.

However, even though single pulse mode of shock tube operation can be achieved by proper adjustments of driver and driven lengths along with the incorporation of dump tank, there is one other issue that needs to be resolved. A close look at Figure 1 reveals that the 'dwell time' experienced by the driven gas sample is the maximum at the end flange and it reduces as the reflected wave travels backwards. One of the reasons is that the expansion fan would be arriving in the opposite direction and it reaches the end flange last. Often the distance between the contact surface and the shock front could be very long, about 1 m in our SPST. The dwell time experienced by the compressed gases in this region varies from the end flange to the contact surface. This has been discussed in detail in our previous publication.[10] This problem is overcome by mounting a ball
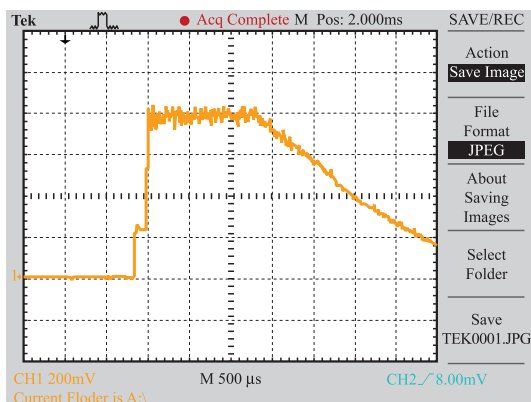

Figure 4: A pressure trace observed in one of the experiments (dwell time = 1320 μs, $T_{5(expt)}$ = 1058 K and P5 = 10.7 Atm).

valve[5] (or a sliding gate valve[11,12]) at a certain distance from the end flange of the driven section. This can produce a third section in the SPST, the test section.

While the gases in the driven section are compressed to about 1 m, the gases in the test section are compressed to within a few cm length from the end flange. A pressure transducer mounted in this region measures the dwell time accurately. All the gases loaded in the test section have nearly uniform reaction conditions. Though the ball valve was originally introduced by Tschuikow-Roux and coworkers in 1970,[13] our group brought the attention back to it in 2002.[5] This approach has now been called as constrained-reaction volume (CRV) strategy, wherein only a small part of the driven section near the end wall is filled with reactive test gas mixture while the rest of the driven section is filled with a nonreactive

or non-explosive mixture.[11,12] Thus, the use of ball valve/sliding gate enables assembling a thin slice of reactive fuel mixture that can be shock heated and made to achieve a near-constant-pressure reaction volume for as long a test time as possible. A concentration profile obtained from 1,2-dichloroethane experiments[14] performed with and without ball valve is shown in Figure 5. It may be observed that around 50% of the gases in the driven section did not experience the reflected shock heating in the absence of ball valve.[14] When we established the CST-1, it was felt that the ball valve was more crucial than the dump tank as the successive reflections are weaker. A dump tank was added later and the shock tube had to be calibrated again.

In principle, all the physical properties behind incident and reflected shock waves can be directly calculated on the basis of the thermodynamic properties of the shocked gas and the measured incident shock velocity. The governing relations for shock wave theory are described by the Rankine-Hugoniot equations, which describe the changes in P and T across a shock front.[3,15] For a kineticist dealing with the thermal effect on chemical decomposition, accurate measurement of the temperature due to shock formation is important to obtain reliable kinetic and mechanistic data. Generally, in majority of the shock tubes, the temperature behind the shock wave is calculated from such standard shock wave relations (a few of such relations are given below):

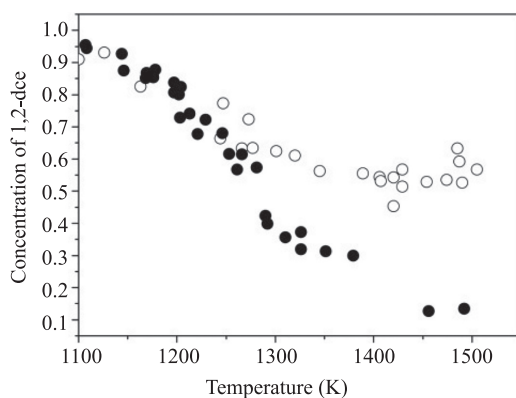$$\frac{P_2}{P_1} = \frac{\{2\gamma M^2 - (\gamma - 1)\}}{\gamma - 1} \tag{1}$$

Figure 5: Concentration profile of 1,2-dichloroethane from experiments performed without ball valve (open circles) and with ball valve (filled circles) ball valve (Ref. 14) (Temperatures are calculated with M_s).

$$\frac{T_2}{T_1} = \frac{[2\gamma M^2 - (\gamma - 1)][(\gamma - 1)M^2 + 2]}{(\gamma - 1)^2 M^2} \tag{2}$$

$$\frac{T_5}{T_1} = \frac{[2(\gamma - 1)M^2 + (3\gamma - 1)][(3\gamma - 1)M^2 - 2(\gamma - 1)]}{(\gamma + 1)^2 M^2} \tag{3}$$

where M = Mach number (= U/a), γ = heat capacity ratio, U = Shock velocity,

a = Sound speed (= $\sqrt{\gamma RT}$), R = Gas constant

However, these equations are based on ideal gas conditions in the shock tube, and the nature and behavior of the shock waves may be valid up to relatively modest pressures. For conditions where the assumptions are valid, the equations can be thought of as describing ideal situations.[16] Thus, the temperature so obtained from such calculations would generally be different from actual temperature experienced by the test gas. Such problems from non-idealities in the shock tube behavior were extensively discussed by Belford and Strehlow[17] in their review article in 1969. They highlighted that such problems are caused by the formation of a boundary layer and its interactions, which in turn, can have serious consequences in the interpretation of experimental results. In practical terms, this comes down to errors in the reaction temperature. Since rate constants usually have an exponential dependence on this variable, there is the possibility of large errors. One approach to circumvent these problems is to calibrate the temperature in terms of the kinetics of a known reaction[1] (termed chemical thermometry); this has been successfully used in single pulse shock tube experiments. This article attempts to highlight the importance of temperature calibration in shock tube for obtaining an accurate kinetic and mechanistic data. A recent calibration study performed in one of our chemical shock tubes that involved the use of ethyl chloride as external standard is also discussed.

3 Chemical Thermometry
In order to obtain reliable kinetic and mechanistic data using shock tube, the temperature in the reaction zone (i.e. T_5) must be accurately known. Accurate determination of T_5 has been achieved with the development of a convenient technique popularly known as 'Chemical thermometric' method; the technique can be 'internal' or 'external' chemical thermometry. In the former case, reflected shock temperature is determined by following the progression of a standard reaction

with a known rate constant, which is investigated together with the reaction of interest. In the latter case, experiments with the standard are done independently, at various temperatures and a calibration curve is drawn between the measured temperature and the calculated one based on the relations given above.[16]

It was Tsang's[18] investigations on the non-ideal temperature effects that led to the development of internal thermometry. By carrying out a simultaneous decomposition of the chemical thermometer and the reagent of interest both species are subjected to identical reaction conditions. The average temperature that is obtained accurately reflects the average temperature experienced by the reagent and minimises the variations inherent from experiment to experiment and deviations from ideal conditions.[16] Thus, it is the error associated with the reported rate coefficient for the decomposition of the internal standard that determines the accuracy of the estimated reflected shock temperatures. The expression used for calculating temperature behind reflected shock wave involving use of internal standard takes the form as given in Eq.(4):

$$T = (-E/R)/\left[\ln\left\{-\frac{1}{A \times t}\ln(1-\chi)\right\}\right], \qquad (4)$$

where t is the reaction dwell time, E and A are the activation energy and pre-exponential factor respectively, for the decomposition of the internal standard used, and χ is the extent of the standard reaction, defined as

$$\chi = [product]_t/\{[product]_t + [internal\ standard]_t\},$$

where $[product]_t$ is product concentration of internal standard at time 't', and $[internal\ standard]_t$ is the left out concentration of internal standard at time "t".

However, there are few limitations in using internal chemical thermometry for the estimation of reflected shock temperatures. The most important one being that the product of the standard reaction should not be a product of the compound under investigation. Also, neither the internal standard nor any of its products should react with the compound under investigation or any of its products.[16] Thus, it becomes obvious that for those high pressure shock tube experiments involving complex mixtures of radical and stable species, the probability of mechanistic interference with the internal chemical thermometer would be high. Consequently, it necessitated the modification of the internal chemical thermometry so as to obtain the real post shock temperature. The modified technique came to be known as external chemical thermometry as mentioned above. The external chemical thermometry also makes use of the same expression given in Eq. (4) for the estimation of temperature behind reflected shock wave. The temperatures so obtained are then plotted against the reflected shock temperatures calculated by conventional Rankine-Hugoniot relations. Least squares fitting of the resulting plot can then be used to determine T_5 for all the experiments. However, it must be noted that although 'external' chemical thermometer method avoids the possibility of cross-reaction, some experiment to experiment variations may be introduced since experimental variations cannot be accommodated the same way as when an internal thermometer is present.[16] Some of the commonly used standard reactions for chemical thermometry are listed in Table 1.

It must also be noted that there may be usage of more than one chemical thermometer for the same experiment so as to cover the required temperature range. An illustrative example in this regard is the use of cyclopropane carbonitrile (c-C$_3$H$_5$CN) and 1,1,1-trifluorethane (CH$_3$CF$_3$) both as internal standards during the study

Table 1: List of commonly used chemical standards for thermometric calibration.

| Sl. No	Chemical Standard: Reactions	Rate expression k_{expt} (sec^{-1})	Working Temperature range (K)	References
1.	Cyclopropane carbonitrile: c-C$_3$H$_5$CN → CH$_3$CH = CHCN c-C$_3$H$_5$CN → CH$_2$ = CHCH$_2$CN	$10^{14.58}$ exp(−57.8/RT)	900–1040	19, 20
2.	Ethyl chloride: CH$_3$CH$_2$Cl → C$_2$H$_4$ + HCl	$10^{13.84}$ exp(−57.8 /RT)	960–1100	5, 13
3.	1,1,1-trifluoroethane: CH$_3$CF$_3$ → CH$_2$ = CF$_2$ + HF	$10^{14.85}$ exp(−74.05/RT) 5.71×10^{46} (T)$^{-9.341}$ exp(−47073 K/T)	1150–1350 1000–1600	16, 19, 21–23 24, 25
4.	Cyclohexene: c-C$_6$H$_{10}$ → C$_4$H$_6$ + C$_2$H$_4$	4.84×10^{14} exp(−63.39/RT)	950–1300	16, 26, 27

of isomerization and decomposition of 1,2-benzisoxazole behind reflected shock waves.[19] Cyclopropane carbonitrile (which isomerizes to cis-and trans-crotonitrile, $CH_3CH = CHCN$ and vinylacetonitrile, $CH_2 = CHCH_2CN$) was used over the temperature range 900–1040 K, while 1,1,1-trifluorethane was used over the temperature range of ~1190–1350 K. Further, mention may be made of study by Sidhu and coworkers[22] on iso-octane ignition under scramjet conditions where they used 1,1,1-trifluorethane, 1-chloropropane and 2-chloropropane as external thermometers as these standards were known to react with hydrocarbon fuels in the covered temperature range of 900–1400 K. Thus, by opting for external calibrations, any impact on the ignition delay that may occur by introducing the chemicals internally was prevented.

4   Recent Shock Tube Calibration Using Chloroethane as External Standard

We have recalibrated the Chemical kinetic Shock Tube (CST1) present in our laboratory[5,6] as the tube has undergone some modifications recently. A dump tank of diameter 100 mm having a length of 1661 mm has been recently connected near to the diaphragm station in the driven section at an angle of 45° to the shock tube facility. The previous temperature calibration data reported in 1,2-dichloroethane study (Refer Table 1 in Ref. 5) were obtained from single pulse shock tube experiments performed without dump tank feature, although rest of the shock tube configurations remain the same. There is large difference between the reflected shock temperatures calculated using Mach number and the external chemical thermometry method reported in this study,

which can be seen in the Table 2. This also gave the motivation to recalibrate the shock tube facility so that the experimental reflected shock temperatures become more accurate.

Hence, the thermal decomposition of 2-chloroethane (external standard) was performed at varying P_4/P_1 conditions in the same chemical shock tube (now with dump tank) with the objective of obtaining a more accurate calibrated reflected shock temperatures. The pyrolysis of the standard sample has been studied for the reflected shock temperatures $(T_{5(Ms)})$ (calculated using shock Mach number) ranging from 981 to 1183 K and P_5 ranging from 7 to 13 atm, while reaction time (dwell time) ranges from 1280 to 1410 μs. An experimental pressure observed during one of the experiments is shown in Fig. 4. In the studied temperature range, it is seen that the HCl elimination channel has been found to be the only thermal decomposition pathway.

$$CH_3CH_2Cl \rightarrow C_2H_4 + HCl$$
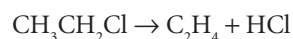
Both the reactant (2-chloroethane) and product (ethene) have been identified and quantified using Agilent Gas Chromatography (Model: 6890 A) having HP5 column installed in it. For quantification purposes, the calibrations of 2-chloroethane and ethene in GC- Flame Ionisation detector (FID) have also been performed separately. The Chromatogram is shown in Fig. 6 identifying the species present in the reaction mixture.

The experimental temperature $(T_{5(kin)})$ for the reaction has been calculated by putting the experimental rate constant values in the Arrhenius expression reported for the same reaction by

Table 2: Temperatures behind reflected shock wave as presented in Table1 in Ref. 5.

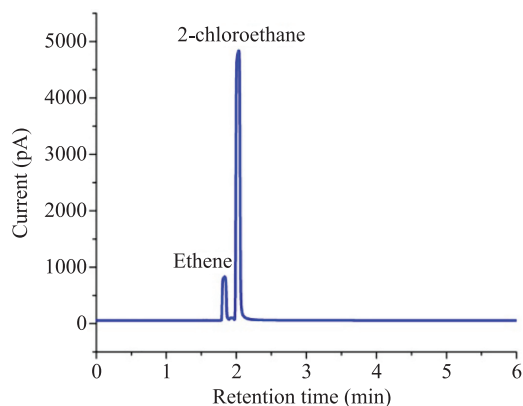| Sl. No.	$T_{5(Ms)}$ (K)	$T_{5(kin)}$ (K)	$T_{5(Ms)} - T_{5(kin)}$ (K)	% (ΔT_5)
1	1068	991	77	**7.77**
2	1094	1024	70	**6.84**
3	1146	1031	115	**11.15**
4	1153	1060	93	**8.77**
5	1157	1061	96	**9.05**
6	1236	1104	132	**11.96**
7	1236	1107	129	**11.65**
8	1261	1125	136	**12.09**
9	1325	1171	154	**13.15**
10	1384	1210	174	**14.38**

Figure 6: Chromatogram showing the separation of 2-Chloroethane and ethene in the GC column (HP5 column), $T_{5(kin)}$ = 1057 K.
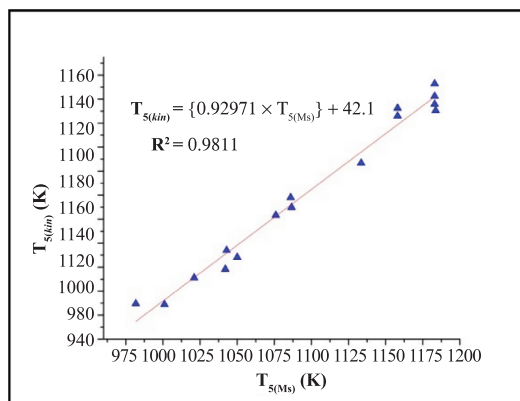

Figure 7: Plot of Experimental T_5 Vs theoretical $T_{5(Ms)}$ showing their correlation within the experimental temperature range 969–1186 K.

Table 3: Summary of the experimental results of 2-chloroethane pyrolysis for T_5 calibration.

Sl. No.	Dwell time (μs)	$T_{5(Ms)}$ (K)	$T_{5(kin)}$ (K)	$[EC]_t/[EC]_0$	$[C_2H_4]_t/[EC]_0$	P_5 (atm)
1	1400	**981.7**	**969.57**	0.99092	0.00908	6.3
2	1380	**1001**	**968.87**	0.99124	0.00876	10.3
3	1370	**1021**	**991.14**	0.98299	0.01701	7.1
4	1370	**1042**	**998.34**	0.97903	0.02097	7.2
5	1350	**1042.9**	**1014.08**	0.96771	0.03229	7.9
6	1360	**1050**	**1008.22**	0.97239	0.02761	10.3
7	1330	**1076**	**1043.32**	0.93028	0.06972	10.8
8	1410	**1086.6**	**1049.85**	0.91291	0.08709	9.1
9	1310	**1086**	**1057.96**	0.90061	0.09939	10.7
10	1390	**1133.5**	**1086.71**	0.79465	0.20535	9.6
11	1380	**1158**	**1125.93**	0.56003	0.43996	10.3
12	1350	**1183.7**	**1130.44**	0.53329	0.46671	10.2
13	1340	**1158**	**1132.49**	0.52002	0.47998	10.2
14	1280	**1183**	**1135.84**	0.50977	0.49023	10.7
15	1360	**1183**	**1142.46**	0.43591	0.56409	9.7
16	1300	**1183**	**1152.81**	0.36876	0.63124	10.4

Tschuikow-Roux et al.[13] for the temperature range of 960–1100K. The effect of temperature on HCl elimination product is shown in the Table 3, wherein it can be seen that the rate of HCl elimination increases with increasing temperature within the temperature range studied.

$$k_{expt} \ (sec^{-1}) = 10^{13.84 \pm 0.20} \exp \left[- (57.8 \pm 1.0 \ kcal/mol)/RT \right]$$

$$T_{expt} = (57.8 \pm 1.0 \ kcal/mol) \ / \ R \times [\{2.303 \times (13.84 \pm 0.20)\} - \ln k_{expt}]$$

The experimental $T_{5(kin)}$ are plotted against $T_{5(Ms)}$ obtained with the reflected shock mach number. The least square fitting of this data has been performed (Fig. 7) to determine experimental T_5, which can be used as the actual experimental temperature for the future experiments that will be performed within the specified temperature range.

The correlation between $T_{5(kin)}$ and $T_{5(Ms)}$ within the Experimental $T_{5 \ (Ms)}$ range of 982–1183 K is found to be:

$$T_{5(kin)} = \{0.92971 \times T_{5(Ms)}\} + 42.1 \quad (R^2 = 0.9811)$$

It can be clearly seen from the above plot that the calculated temperature, $T_{5(Ms)}$, overestimates the actual temperature, $T_{5(kin)}$, and the difference increases with increasing temperature. The reflected shock temperatures calculated using Mach number, $T_{5(Ms)}$, and that obtained from the measurement of extent of ethyl chloride decomposition, $T_{5(kin)}$ differed by ~1.3–4.5% in the calibrated temperature range. This result is quite an improved data when compared to the calibrated data reported previously in 1,2-dichloroethane study where the corresponding percentage variation was around 8–14%. The higher discrepancy (between the two temperatures) observed at the higher temperatures is obviously expected as the T_5 calculation using conventional Rankine-Hugoniot relations does not account for the non-idealities in the reflected shock wave.

5 Conclusion

A brief review on importance of temperature calibration of shock tube using chemical thermometric method has been presented. Use of the common chemical standards such as cyclopropane carbonitrile, 1,1,1-trifluoroethane, cyclohexene, and ethyl chloride, in various kinetics studies have been highlighted. In general, it is seen that the $T_{5,deal}$ generally overestimates the $T_{5,real}$, which is the result of the assumptions involved in calculating ideal T_5. The recent temperature calibration study (performed using ethyl chloride as external standard) also showed that the calculated reflected shock temperature $T_{5(Ms)}$ exceeds the kinetic $T_{5(kin)}$ by around 1.3–4.5% in the temperature range of 982–1183 K. Thus, chemical thermometry method (internal or external) removes natural uncertainties in the experimental conditions, thereby eliminating the uncertainty in the measurement of temperature and hence, rate parameters. Finally, it can be said that the internal standard method in general serve the purpose (temperature calibration) better, which is due to the fact that both the internal standard and reactant molecule experience the same reaction conditions (provided the use of method is feasible and that no cross reaction(s) occur).

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