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Rate Coefficient for $H+C_2H_2 \rightleftarrows C_2H+H_2$

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Synopsis. The rate coefficient expressions $k=10^{13.78}$ exp(−99 kJ/*RT*) cm^3 mol^{-1}s^{-1} for $H+C_2H_2 \rightarrow C_2H+H_2$ and $k=10^{13.05}$ exp(−12 kJ/*RT*) cm^3 mol^{-1} s^{-1} for $C_2H+H_2 \rightarrow H+C_2H_2$ were proposed after correcting for errors in previously reported data analyses of shock tube data on C_2H_2 pyrolysis.

The homogeneous thermal decomposition of C_2H_2 proceeds by chain reactions in which one of the important elementary reactions is

$$H + C_2H_2 \longrightarrow C_2H + H_2. \qquad (1)$$

Rate coefficients for this reaction can be derived by analysing C_2H_2 decomposition rate data with the aid of computer modeling. In one of such studies, Tanzawa and Gardiner[1] (TG1) fitted laser-schlieren profiles of the density gradients in C_2H_2–Ar mixtures heated by incident shock waves to temperatures in the range 1700—3400 K. In another, Koike and Morinaga[2] (KM) fitted 216 nm absorption profiles of C_4H_2 appearance from C_2H_2–Ar mixtures heated to temperatures in the range 1800—2600 K in incident shock waves. In a modeling study in which a number of experiments were interpreted with a single mechanism[3] (TG2), a temperature-independent value for the rate coefficient of the reverse reaction $k_{-1}=10^{13.54}$ cm^3 mol^{-1} s^{-1} was reported to fit the experimental results. This value is higher than the k_{-1} value $10^{12.4}$ cm^3 mol^{-1} s^{-1} of KM by a factor much larger than the anticipated experimental error bounds. In order to discover the source of this difference, the procedures used in both data analyses were reexamined. As described below, the apparent discrepancy resulted from transcriptional errors in manuscript preparation and in an incorrect thermochemical data record for C_2H. When these corrections were made, it became clear that the KM and TG1 experiments are in close agreement about the rate of Reaction (1).

For the conditions of C_2H_2 decomposition in shock waves, Reaction (1) proceeds in the forward direction during the time of rate measurements. In the data analysis of TG2, the forward rate coefficient k_1 was input as an Arrhenius expression for the computer modeling. As it was noticed that this expression implied fairly constant values of the reverse rate coefficient k_{-1}, it was decided to report a temperature-independent k_{-1} valid for the range of the TG1 experiments rather than the Arrhenius expression of k_1. (The computer programs used in all studies discussed here used essentially identical mathematical procedures and include both the forward and reverse directions of all reactions, the reverse reaction rate coefficients being computed from the forward reaction rate coefficients using the equilibrium constant implied by the thermochemical properties of the reacting species.) Unfortunately, in preparing the TG2 manuscript for publication, the preexponential factor of the k_1 expression $10^{13.54}$ cm^3 mol^{-1} s^{-1} was assigned to k_{-1} instead of the value $10^{12.75}$ cm^3 mol^{-1} s^{-1} that was actually found to be typical of the k_{-1} values implied by k_1 expressions that provided good fits to the TG1 data.

In analysing their data, KM adopted the more convenient reverse reaction $C_2H+H_2 \rightarrow H+C_2H_2$ as input even though the direction in which reaction proceeded during their measurements was $H+C_2H_2 \rightarrow C_2H+H_2$ as in the TG1 experiments. By adjusting k_{-1} to fit their data, the value $k_{-1}=10^{12.4}$ cm^3 mol^{-1} s^{-1} was found to be optimal, still a factor of two smaller than the corrected TG2 value and still outside the error limits of both studies. The source of the remaining discrepancy was found on investigation to be a faulty thermochemical data record for the species C_2H. While this record was faulty at first in both the TG2 and KM computer programs, it affected the data analysis only through computing the value of k_1 from k_{-1}, and thus distorted only the KM computations. When the correct C_2H thermochemistry was used, it was found that the optimal k_{-1} values for fitting the KM data became quite close to the corrected TG2 result. Over 2000 K, $k_{-1}=10^{12.88}$ cm^3 mol^{-1} s^{-1} gave very close match to the KM data, while at lower temperatures $k_{-1}=10^{10.18}$ exp(115 kJ/*RT*) was required. A comparison with the KM data is shown in Fig. 1. It can be seen that the inconsistent k_{-1} expression for lower temperatures is actually very close to higher-temperature result; There seems to be some unappreciated systematic error at lower temperatures, which has no effect upon the analysis presented here. Arrhenius expressions can be derived for k_1 and k_{-1} by combining room temperature

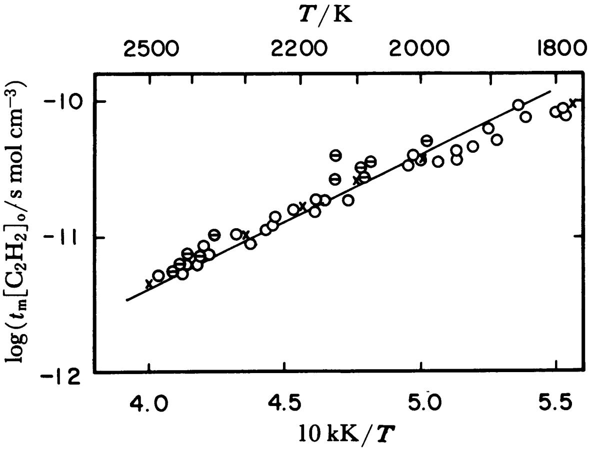

Fig. 1. Comparison of computed and measured rate parameters for 216 nm absorption change. For definition of t_m, see Ref. 2.
○: C_2H_2/Ar=3.2/96.8, ⊖: C_2H_2/H_2/Ar=2.0/2.2/95.8, and ×: computed for C_2H_2/Ar=3.2/96.8. All data points are from Ref. 2.

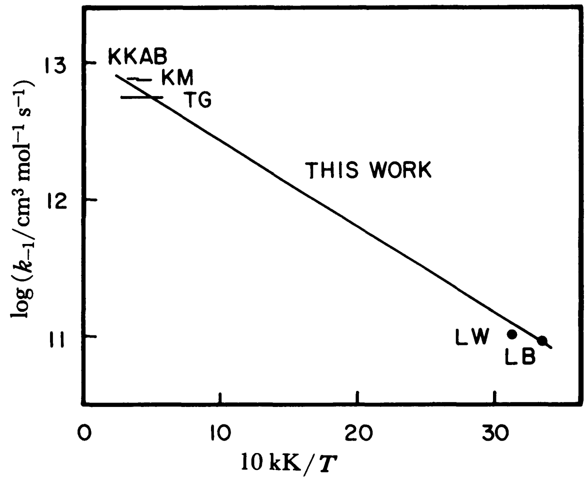

Fig. 2. Arrhenius graph for $C_2H+H_2\rightarrow C_2H_2+H$. KKAB=Ref. 11, KM=Ref. 2, TG=Ref. 1, LW=Ref. 4, LB=Ref. 5, and THIS WORK=$10^{13.05}$ exp(-12 kJ/RT) cm^3 mol^{-1} s^{-1}.

measurements of k_{-1} with a representative value for k_{-1} at 2800 K of $10^{12.75}$ cm^3 mol^{-1} s^{-1}. Lange and Wagner[4] reported $k_{-1}=10^{11}$ cm^3 mol^{-1} s^{-1} at 320 K, while Laufer and Bass[5] reported $10^{10.96}$ cm^{3}mol^{-1} s^{-1} at 298 K. The Arrhenius expression $k_{-1}=10^{13.05}$ exp(-12 kJ/RT) cm^3 mol^{-1} s^{-1} accounts for the 50-fold increase in rate coefficient between 300 and 2800 K. (Fig. 2) The corresponding expression for k_1 is $10^{13.78}$ exp(-99 kJ/RT) cm^3 mol^{-1} s^{-1}. These two expressions are thermochemically compatible with one another providing that JANAF[6] thermochemistry is used for all species except that $\Delta H^\circ_{f0}(C_2H)=531$ kJ/mol as derived by Okabe and Dibeler.[7]

The only other study known to us in which fairly direct determination of k_1 or k_{-1} is asserted is that of Yampol'skii *et al.*[8] Their expessions, however, are more than an order of magnitude higher than the consensus of the 5 studies shown in Fig. 2, and apparently result from contamination by unidentified catalytic pathways for isotope exchange.

Aside from Reaction (1), the reaction mechanisms used by KM and TG2 differ in that TG2 included the reaction

$$H + C_2H_2 \longrightarrow C_2H_3 \qquad (2)$$

using a rate coefficient reported by Payne and Stief,[9] while KM used instead the M-dependent form for the reverse reaction

$$C_2H_3 + M \longrightarrow C_2H_2 + H + M \qquad (-2)$$

and a theoretical rate coefficient derived by Benson and Haugen.[10] While reactions of C_2H_3 become important in C_2H_2 thermal decomposition only at temperatures well below those of the TG1 and KM experiments, we nonetheless repeated the TG2 computations using Reaction (-2) and the Benson and Haugen rate coefficient expression. No significant differences were seen. We note, however, that while the rate of Reaction (2) is predicted to be more or less the same by both the Payne and Stief and the Benson and Haugen expressions for the conditions of the TG1 and KM experiments, they do diverge for other conditions and must be adopted with care for simulation purposes.

Subsequent to the TG2 and KM publications, the thermal decomposition of C_2H_2 produced from thermal decomposition of C_2H_4 was studied by Kiefer *et al.*[11] For their conditions, Reaction (1) proceeds predominantly in the reverse direction, and the laser-schlieren gradients they measured proved to be sensitive to k_{-1}. Their result $k_{-1}=10^{12.87}$ cm^3 mol^{-1} s^{-1}, for the temperature range 2600—3000 K, is seen to be in good agreement with the expression derived here. Reference is made to their paper for extensive discussion of the effect of subsequent reactions for their and the TG1 experimental conditions.

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References

1) T. Tanzawa and W. C. Gardiner, Jr., "17th Int. Symp. Combust.," The Combustion Institute, Pittsburgh (1979), p. 563.

2) T. Koike and K. Morinaga, *Bull. Chem. Soc. Jpn.*, **54**, 530 (1981).

3) T. Tanzawa and W. C. Gardiner, Jr., *J. Phys. Chem.*, **84**, 236 (1980).

4) W. Lange and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.*, **79**, 165 (1975).

5) A. H. Laufer and A. M. Bass, *J. Phys. Chem.*, **83**, 310 (1979).

6) D. R. Stull and H. Prophet, "JANAF Thermochemical Tables," 2nd Ed., NSRDS-NBS 37 (1971).

7) H. Okabe and V. H. Dibeler, *J. Chem. Phys.*, **59**, 2430 (1973).

8) Yu. P. Yampol'skii, K. P. Lavrovskii, Yu. V. Masksimov and V. M. Rybin, *Kinetics and Catalysis*, **15**, 9 (1974).

9) W. A. Payne and L. J. Stief, *J. Chem. Phys.*, **64**, 1150 (1976).

10) S. W. Benson and G. R. Haugen, *J. Phys. Chem.*, **71**, 1735 (1967).

11) J. H. Kiefer, S. A. Kapsalis, M. Z. Al-Alami, and K. A. Budach, *Comb. Flame*, **51**, 79 (1983).