# Isotope Effects on Flame Speeds for Hydrogen and Deuterium

By P. GRAY* and D. B. SMITH†

(*School of Chemistry, The University of Leeds; †Houldsworth School of Applied Science, The University of Leeds)

DIFFERENCES in reactivity arising from isotopic substitution are well known in isothermal systems, being greatest in substitutions involving hydrogen. In combustion, however, there is very little information available on the effects of replacing hydrogen by deuterium, although laminar flame speeds have been measured[1] in $H_2 + Br_2$ and $D_2 + Br_2$ mixtures. Accordingly, burning velocities have been measured in the four systems $H_2 + O_2$, $D_2 + O_2$, $H_2 + N_2O$, and $D_2 + N_2O$. Details of the experimental method have been given previously[2]: measurements of the flame speed relative to the burnt gas ($S_B$) were carried out in a closed vessel at sub-atmospheric pressure (initial pressure, 70 mm. Hg, initial temperature 62 $\pm$ 2°c). The results of the measurements are displayed in Figures 1 and 2.

For the $H_2 + O_2$ and $D_2 + O_2$ systems, the flame speeds differed over the whole composition range, being always greater for hydrogen mixtures. The maximum values for $S_B$ occurred in slightly lean mixtures (64—65% fuel) and were ca. 4180 cm. sec.$^{-1}$($H_2$) and ca. 3030 cm. sec.$^{-1}$ ($D_2$). The average value for the quotient ($S_B$ in $H_2$ mixture)/($S_B$ in $D_2$ mixture) was ca. 1·4 being somewhat exceeded (quotient ca. 1·53) in mixtures near the rich limit.

For $H_2 + N_2O$ and $D_2 + N_2O$ mixtures, a similar pattern was observed, hydrogen flames again being faster. Maximum speeds occurred in slightly rich mixtures (53% fuel) and were ca. 3470 cm. sec.$^{-1}$($H_2$) and ca. 2740 cm. sec.$^{-1}$($D_2$). The value for the quotient of flame speeds was ca. 1·3 over most of the range, again rising a little (to 1·43) near the rich limit.

There is little previous work on the effects of isotopic substitution in these systems. Composition limits of flammability for $H_2 + O_2$ and $D_2 + O_2$ have been determined[3] by Payman and Titman, Clusius and Gutschmidt, and Clusius and Faber. The flammable range is wider for hydrogen mixtures than for deuterium. The ratio of the percentage of hydrogen to the percentage of deuterium in the respective lean-limit mixtures, reported by different workers varied, but was ca. 1·35. The rich limits, however, were very similar for the two systems. No flammability limits have been reported for $D_2 + N_2O$ mixtures.

In spontaneous ignition, the second (upper) explosion limits have been determined[4] for $H_2 + O_2$ and $D_2 + O_2$ mixtures. The limit (expressed as total pressure) is higher for deuterium than for hydrogen. This limit is determined by the efficiencies with which collisions can stabilize the excited species, $HO_2*$ or $DO_2*$. Although hydrogen and deuterium have the same efficiency per collision in stabilizing $HO_2*$ and $DO_2*$, on account of its greater mass and lower speed, deuterium makes fewer collisions per second. Thus, deuterium is less successful in stabilising $DO_2*$, than $H_2$ is in stabilizing $HO_2*$.

The only other previous work concerns the isothermal reactions. Hinshelwood, Williamson, and Wolfenden,[4] and Melville[5] found that in the temperature range 250—560°c, hydrogen reacted more rapidly with oxygen than deuterium did. The superior reactivity of hydrogen was ascribed to its greater zero-point energy. For the reaction with nitrous oxide, Melville found[5] that in the range 250—400°c hydrogen and deuterium reacted at the same rate. In these cases, the reactions $H + N_2O$ and $D + N_2O$ are the rate-determining steps, and
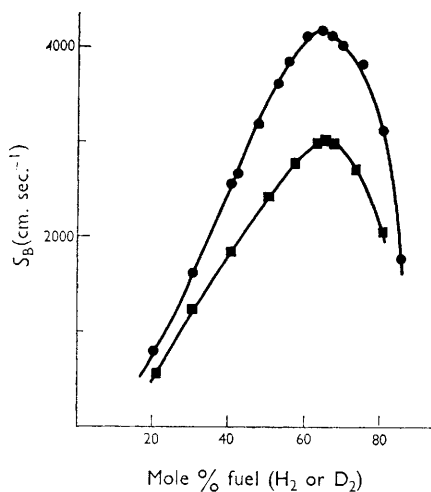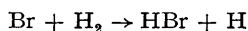
FIGURE 1. Composition-dependence of flame speed relative to burnt gas ($S_B$) at 70 mm. Hg., for $H_2 + O_2$ and $D_2 + O_2$ mixtures. (◯$H_2$, ✕$D_2$)



FIGURE 2. Composition-dependence of flame speed relative to burnt gas ($S_B$) at 70 mm. Hg., for $H_2 + N_2O$ and $D_2 + N_2O$ mixtures. (◯$H_2$, ✕$D_2$)

they will show no zero-point energy effect as deuterium is substituted for hydrogen. Although a difference in rates might still have been expected to arise from different collision frequencies (ratio of collision frequencies between H and $N_2O$, and D and $N_2O$ is $\sqrt{2}$), hydrogen atoms also diffuse to the walls $\sqrt{2}$ times faster than deuterium atoms and chain termination occurs there. The net result is that no separation in rates is observed.

All previous work demonstrates that hydrogen is chemically more reactive than deuterium, and it is certain that its enhanced reactivity influences the flame speed. For hydrogen + bromine flames, Gilbert and Altman,[6] using the results of Cooley and Anderson,[1] correlated the change in burning velocity that occurred when hydrogen was replaced by deuterium, with the difference in the rates of the elementary reactions supposed to be rate determining.

$$Br + H_2 \rightarrow HBr + H$$

$$Br + D_2 \rightarrow DBr + D$$

In the present systems, differences in flame speeds as hydrogen is replaced by deuterium are to be sought in differences in reactivity and transport properties. If the flame speed can be correlated with the rate of a single elementary reaction in which an H–H or D–D bond is broken (such as $O + H_2 \rightarrow OH + H$), the change from deuterium to hydrogen is expected to be accompanied by a decrease in activation energy arising from a zero-point energy difference of 1·82 kcal. mole$^{-1}$. At
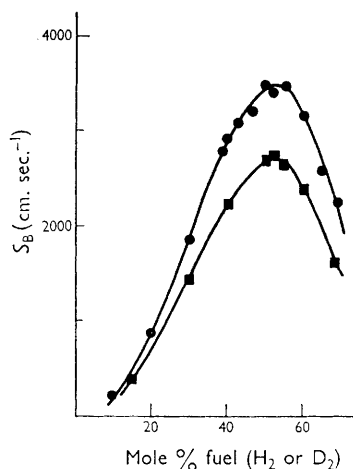
the temperatures found in the flame zone (2500—2700°K), this can contribute a 1·42-fold increase in the reaction rate. In addition, the collision frequency and hence the pre-exponential factor are increased by a factor of $\sqrt{2}$. The net result is an expected increase in rate of about 2, when hydrogen is substituted for deuterium. In turn, flame speeds which are proportional to the square root of the average rate, are expected to increase by a factor of ca. 1·42.

The influence of thermal conductivity may also be estimated roughly. Our own measurements[7] show that the ratio of the thermal conductivity of a stoicheiometric $H_2 + O_2$ mixture to that of a stoicheiometric $D_2 + O_2$ mixture is 1·40 between 50° and 100°. In the flame zone, although the $H_2O$ and $D_2O$ are dominant, there are appreciable concentrations (up to 25%) of atomic and molecular hydrogen or deuterium, and the thermal conductivity in the $H_2 + O_2$ flame zone is expected to be about 1·27 times greater than that in the $D_2 + O_2$ flame. Since flame speed is proportional to the square root of thermal conductivity, the greater thermal conductivity of hydrogen will increase the flame speed by a factor of about 1·13. For $H_2 + N_2O$ and $D_2 + N_2O$ flames, the expected thermal conductivity ratio is about 1·20, leading in turn to a 1·1-fold increase in flame speed.

Thus the possible isotope effect in these flames is about 1·6 for $H_2 + O_2$ and $D_2 + O_2$ mixtures, and about 1·56 for $H_2 + N_2O$ and $D_2 + N_2O$ mixtures: observed isotope effects are 1·4 and 1·3 respectively. The estimated value for the $H_2 + O_2$ system is too

large, because the correlation of flame speed with the rate of a single elementary reaction is an over-simplification. The difference between the observed and estimated values for the isotope effect arises from the contribution of other types of elementary reactions (such as $H + O_2 \rightarrow OH + O$) which are known to play a part.[8] Reactions of this type, in which no H–H or D–D bond is broken, have smaller isotope effects, and would give rise to smaller changes in flame speed.

The same explanation (in terms of the participation of reactions without H–H or D–D bond rupture) serves for the case of the nitrous oxide systems. For these flames, the reactions $H + N_2O \rightarrow N_2 + OH$ or $D + N_2O \rightarrow N_2 + OD$ are known[8] to be very important. If they alone controlled the flame, the expected magnitude of the isotope effect would be 1·3. While the exact agreement thus produced between observation and expectation is probably fortuitous, the correlation is surprisingly good.

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