

CHEMICAL REACTIONS in SHOCK TUBES

By E. F. Greene

From the 20th to the 22nd of April 1964, 85 chemists and physicists from England, Germany, Japan, Canada, and the United States gathered on the campus of Duke University for a symposium on chemical reactions in shock tubes. This meeting served to outline clearly both the contributions which shock tubes have made to chemical research and the prospects which may be anticipated in the near future.

In the years following World War II, many people began studies of fast chemical reactions and high-temperature phenomena. In this work, shock tubes played a prominent part because they offered an easy way to produce uniform and extremely rapid heating of gas samples to temperatures of many thousand degrees Kelvin.

The first enthusiasm for this work was tempered by the realization of many difficulties which were associated with the technique. Boundary layers on the shock-tube walls brought troublesome deviations from one-dimensional flow, particularly when reflected shock waves were used. The directly measured quantities, such as the electrical conductivity or absorption of light, were frequently not easy to relate accurately to the concentrations of chemical species. There was further the disconcerting scatter of the results for what was presumably the same process measured in different laboratories, or even in the same apparatus by the same man. Perhaps most important of all for chemical kinetics was the clear demonstration once again that the measurement of one quantity, such as the concentration of one species, left far too much latitude in the interpretation of the experiments in terms of a chemical reaction mechanism.

The papers and discussion at the symposium

showed that substantial progress has been achieved in overcoming many of these problems. Because a discussion of all the papers presented would extend this report unreasonably, the author has chosen instead to describe a few examples selected from the group of contributions which seemed to him to be especially significant.

M. Camac (AVCO) reported some preliminary thickness measurements for Ar and N₂ over the range of Mach numbers from 3 to 10. He used a 61-cm-diameter shock tube which permitted operation at initial pressures down to 0.03 torr. He obtained his density profiles by sending a collimated beam of 90-keV electrons parallel to the shock front and then recording the scattered intensity at a few degrees from the incident beam. The shock thicknesses he reported for Ar varied from 4 λ_1 to 5 λ_1 and those for N₂ from 3 λ_1 to 4 λ_1 over the Mach number range 3 to 10. Here λ_1 is the mean free path before the shock. No previous experiments have been carried out above Mach 5.

K. L. Wray (AVCO) also reported shock thicknesses measured in the same shock tube, but he, together with T. S. Freeman, studied O₂ by its ultraviolet absorption and covered the larger Mach-number range of 4 to 21. They were interested particularly in the coupling of rotational and vibrational relaxation with the chemical dissociation. For Mach numbers lower than 10 only the translation and rotational degrees of freedom absorb energy in the shock front. By Mach 14, however, vibrational relaxation, and by Mach 17, dissociation, are also taking place in the front. At these extreme temperatures (20 000°K), there is no longer any possibility of considering an ordering and separation of relaxation processes with rota-

The use of shock tubes in the study of high-temperature phenomena and fast chemical reactions has created a research area with problems of mutual concern to physicists and to chemists. The symposium summarized here (for which no formal publication of proceedings is planned) was held under the sponsorship of the United States Army Research Office in Durham, N. C. E. F. Greene, the author of this report, is professor of chemistry at Brown University.

tion preceding vibration, and it in turn preceding dissociation.

It is also worth noting that the work of Camac and Wray and Freeman provides the most direct measurements of shock-wave density profiles which have been achieved up to now in any Mach-number range.

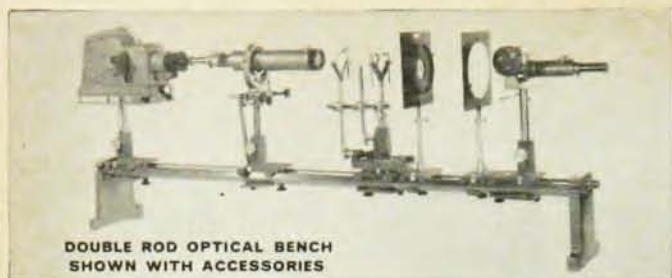
In principle, a continuous record of the concentrations of all the products formed behind a shock wave should give the least ambiguous information about the reactions occurring in the hot gas. The difficulty has been in getting a truly representative sample for analysis. R. W. Diesen (Dow) described his recent studies of the decomposition of N_2F_4 and NF_3 . A portion of the gas heated by a reflected shock flowed through a 0.05-mm-diameter hole in the end plate and then into a mass spectrometer which yielded spectra every 25 μ seconds. Time histories of the concentrations of NF , NF_2 , F , NF_3 , and N_2 over the temperature range 1200-3000°K were very helpful in selecting a mechanism for the reaction. Although there are still some uncertainties in the sampling, and an internal standard such as an inert gas is generally used, the technique seems very promising. A. Modica (AVCO) reported his work at Princeton with D. F. Hornig on the same reaction at much lower temperatures (350-450°K). The precision of these results was impressive, and they could be explained convincingly in terms of the reaction $N_2F_4 + M \rightleftharpoons 2NF_2 + M$.

When the chemical reaction products generated in a quenched shock wave are collected for analysis, as with a gas chromatograph, there is no chance of detecting the unstable species which react with each other during the cooling. Nevertheless, an analysis can be made for all the chemically

stable products. Thus, under favorable conditions, the complex set of reactions, which take place in a chemically reactive mixture subjected to a shock, can be successfully inferred. As in many other shock-tube studies, the temperature of the gas is difficult to specify, so that the rate constants which are deduced apply to a somewhat inaccurately known temperature. S. H. Bauer (Cornell) reported several studies of this kind and emphasized particularly the work of W. Tsang (NBS) who has been able to obtain remarkable accuracy by using the shock heating only to provide relative rates for two reactions taking place simultaneously in the same shock. His comparisons of the rates of similar reactions, such as the unimolecular decompositions of *t*-butyl chloride and *t*-butyl bromide, have allowed him to obtain rates for a large group of reactions which are internally consistent to within 0.1 kcal/mole for the activation energies. His extrapolated values also agree well with earlier results at room temperature. Because the uncertainty in the temperature history of the sample has a very small effect on the relative rates, this technique promises to provide a large body of kinetic information over a wide temperature range, but still promises to retain the high level of accuracy which one expects for measurements in the liquid phase near room temperature.

Most kinetic studies in shock tubes are still being carried out by following the emission or absorption of light at one or more frequencies which are suitable for detecting particular species. Much of this work is now concerned with triatomic molecules. The decomposition of SO_2 has been studied at three different laboratories under different conditions and has yielded strikingly different activation energies. At Imperial College, Gaydon, Kimbell, and Palmer observed the increase in the concentration of SO from its ultraviolet absorption and found an apparent activation energy, $E_a \approx 56$ kcal/mole. Levitt (Imperial College) followed the emission at 4400 Å and obtained $E_a = 73$ kcal/mole. Jost and Wagner (Göttingen) reported work in which the SO_2 was much more highly diluted with Ar and for which E_a was approximately 110 kcal/mole. Although Palmer (Penn State) was able to suggest a mechanism which is consistent with these results, some further study seems advisable.

Combustion reactions have always attracted attention in chemical kinetics because of their importance and complexity. In this work shock waves provide a useful alternative to studies with flames.



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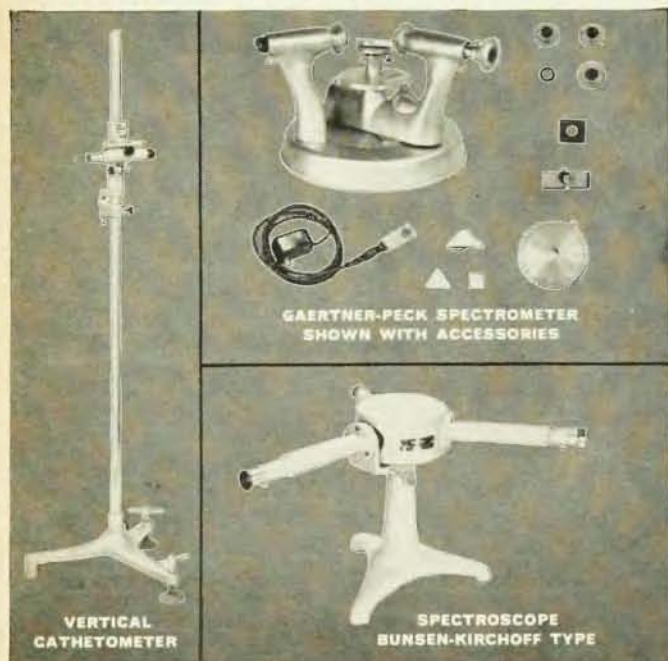
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K. G. P. Sulzmann and B. F. Myers (General Dynamics) reported a very careful study of the formation of CO_2 from CO and O_2 . They recorded the emission from the reacting mixture at three wave lengths and took particular pains to exclude impurities. Nevertheless, the interpretation of the induction period for the formation of CO_2 remains somewhat in doubt. In addition, the mechanism of the oxidation of hydrocarbons continues to be the object of much study. Gardiner (Texas), Miyama (Toyo Rayon), and Glass and Michaels (Harvard) described some of their recent work which has been devoted to improving our understanding of this complicated problem.

The structure of the reaction zone in gaseous detonations has been studied for a long time. Much of the complication arises because, in ordinary self-sustaining detonations, the flow is not laminar but turbulent. These distortions of the front are very clearly shown on interferograms taken by D. R. White (General Electric). White has also been able to produce a transient, laminar detonation by expanding the flow around a corner. For $\text{H}_2\text{-O}_2$ mixtures the principal reaction during the induction period yields H_2O and O , and the subsequent release of heat is due largely to the recombination of O atoms. This is consistent with available kinetic data from other sources. Both H_2 and O_2 appear to undergo rapid vibrational relaxation, and the measured maximum densities agree with those predicted on the basis of the Döring, Zel'dovich, von Neumann model for reactants which are vibrationally equilibrated but unreacted.

Throughout the symposium, from the welcoming remarks by Col. N. M. Bengtson to the last discussion period, everything ran smoothly thanks to the careful preparation and thoughtful organization of D. R. Squire and G. Wyman of ARO(D). It was a model which other meetings can aim to match. There were no registration forms, there was a banquet with no speeches; no proceedings will be published. There were no parallel sessions, and plenty of time was left for discussion. The audience responded enthusiastically with comments and questions. The support of ARO (D) helped to make this a truly international gathering by making possible the attendance of several foreign participants.

The symposium provided for all of us an excellent chance to meet new people with similar interests and to learn about their work at first hand. It also indicated clearly several directions which chemical research with shock tubes may take with profit. This is just what a successful meeting should do.