JOURNAL OF SOLID STATE CHEMISTRY 55, 239–242 (1984)

Application of Continuously Recorded Time-Resolved Mass Spectrometry to the Study of Thermal Explosions

TONG B. TANG, G. M. SWALLOWE, AND V. KRISHNA MOHAN

Physics and Chemistry of Solids, Cavendish Laboratory, Madingley Road, Cambridge CB3 OHE, United Kingdom

Received February 29, 1984; in revised form June 11, 1984

Experimental

Continuously recorded time-resolved mass spectrometry has recently been employed in studies of thermal decomposition of explosives, both primary and secondary (*1, 2*). The data was displayed on an oscilloscope and consecutive scans were recorded on videotapes. The samples were in the powder form and superimposed on the steady decomposition, explosions of individual grains were detected. The time resolution of the recorded mass scans was 20 msec, as dictated by the equipment used. On the other hand, taking 100 μm and 1 km sec^{-1} as the orders of magnitude for the grain size and the reaction propagation velocity (which will be a significant fraction of the steady-state detonation velocity), we see that the time span of each explosion should be around 0.1 μsec $\ll$ 20 msec. Thus, as far as the spectral output is concerned all the molecules involved have fragmented simultaneously or "coherently." Therefore, if reaction intermediates of high vapor pressure and lifetimes not much shorter than 20 msec are considered, they should be recorded in the order they are formed in the decomposition reaction. In general, mass peaks corresponding to daughter species would not appear on the preceding spectrum containing the parent species although, unavoidably, such coherency is reduced after many reaction steps have occurred. That is, later spectra necessarily become more convoluted, owing to the statistical distribution of the lifetimes of the metastable species themselves. Nevertheless, we shall show with the example of mercury fulminate that unambiguous results can be obtained and the reaction scheme may be constructed in a direct way.

$Hg(CNO)_2$ serves as a primary explosive in detonating caps. There is, moreover, considerable interest in the physicochemical properties of metallic fulminates. The main reason is that the CNO^- ion is isoelectronic with the azide ion, N_3; while still being linear and of $C_{\infty V}$ symmetry (*3*), the former is structurally more complicated than the latter, which itself represents a small step toward complexity from halide ions. The gaseous products evolved during the slow thermal decomposition of

0022-4596/84 $3.00

$Hg(CNO)_2$ were identified with mass spectrometry by Boddington and Iqbal (*4*), who also determined the reaction kinetics by monitoring the total pressure as a function of time. The kinetics have been reexamined with use of thermogravimetry (*5*).

In this work the intermediate steps in the reaction were determined for the first time. Powder samples of the fulminate were heated inside a shielded furnace in an ultrahigh vacuum system, which was continuously evacuated by an ion pump. Mass spectra were recorded with a quadrupole instrument (Vg Micromass QX-200) operating at its full mass range of 1–200 a.m.u. and its highest scan rate of 1 a.m.u. per 0.15 msec. The signal from its electron multiplier was fed directly to an oscilloscope (Tektronix 7704A). The short-persistence phosphor screen was filmed with a video camera (JVC GX-88E) interfaced with a videocassette recorder (Akai VS-10 EK) running at a fixed speed of 50 fields/sec. The spectra thus stored were later viewed at the slow replay speed and selected individual spectra could be photographed with the help of "pause" and "single frame advance" facilities available on the recorder. *Two interlaced fields are represented on each of the frames photographed for further analysis. No attempt was made to synchronize the spectrometer and the camera scans so that each frame contains one complete mass spectrum plus a rewrite over one-third of the frame.*

In each experiment the sample was heated to 430 K. At this temperature it was found that explosions occurred intermittently, but not so frequently that more than one event overlapped within such time intervals that their respective mass peaks were present on the same spectrum. Successive runs were made with the electron energy of the spectrometer set at various values from 14 to 18 eV, in case any peaks disappeared at a relatively high ionization voltage because of electron-impact fragmentation of the species, or because on the contrary the electron energy was insufficient to ionize the species (*6*). At the voltage of 15.5 V all peaks were seen to be present and, at this setting, spectra were recorded separately in the two mass ranges of 1–100 and 100–200 a.m.u., so that the positions of transient peaks could be more sharply determined. At the scan speed of 1 a.m.u. per 0.3 msec, the mass resolution was found to remain better than 25% valley. Lastly, spectra of stable species were obtained at a lower speed of 1 a.m.u. per 3 msec; the higher mass resolution thus resulting allowed an accurate measurement of the positions of stable peaks, which acted as calibration markers.

Results

Illustrative sequences of spectra recorded are presented in Figs. 1 and 2. In Fig. 1 frame (a) is the background. The second frame shows the earliest stages of an explosion: a new peak is seen at $m/e = 84$, in addition to an increase in the intensity of the peak at $m/e = 44$. These peaks are assigned to $(CNO)_2$ and N_2O, respectively. The former breaks down into the more stable species of C_2N_2O, C_2N_2, N_2O, NO, N_2, and CN, as is evident from the next spectrum depicted in (c). The transient nature of the dimer $(CNO)_2$ is apparent from the dramatic decrease in its intensity between the two successive spectra, namely (c) and (d). Its exclusive appearance before all other reaction products except N_2O indicates that the cleavage of the Hg–C bond is the primary step in the fast decomposition. The subsequent processes include: (i) cluster formation of the CNO moiety (*4*); (ii) breakdown of $(CNO)_2$ into mostly C_2N_2O, O, N_2O, and presumably C, as is clear from Fig. 2b, and (iii) further fragmentation of C_2N_2O to give rise to final gaseous products listed in the scheme below. In addition to these main pathways, secondary reactions

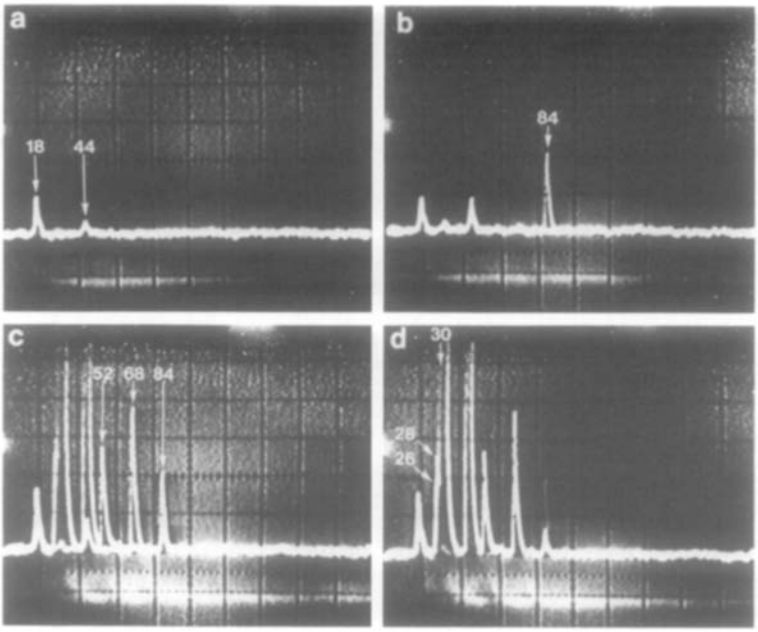

FIG. 1. Spectra taken (a) before, and (b to d) during thermal explosion of mercury fulminate. Mass scan range is 1–200 a.m.u. and interfield time is 20 msec. *There are two interlaced fields represented in each frame.*

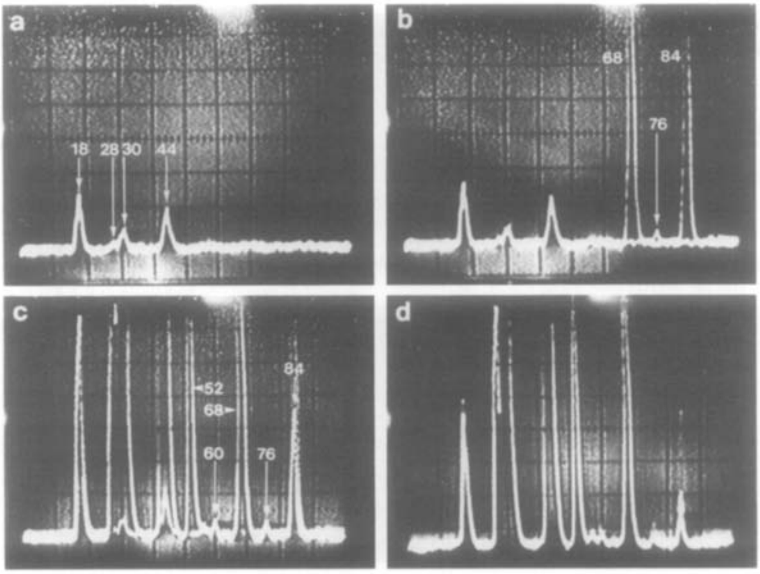

FIG. 2. Spectral sequence (20 msec between *fields*) recorded with a mass scan range of 1–100 a.m.u.

also take place accounting for the presence of certain peaks of low relative intensity that are *identified* in Fig. 2c. Assignments to such peaks cannot be made with certainty. For example, the peak at $m/e = 76$ could be due to C_4N_2 and the species with $m/e = 60$ might be $(NO)_2$.

Proposed Decomposition Scheme

$$\begin{tikzcd}
Hg(CNO)_2 \arrow[r] & Hg + 2CNO \arrow[d] & \\
 & (CNO)_2 \arrow[r] & C_2N_2O,\ O,\ N_2O,\ C_2N_4 \arrow[d] \\
 & & C_2N_2,\ N_2O,\ CO_2,\ NO,\ N_2,\ CN
\end{tikzcd}$$

Conclusions

A method of continuously recorded dynamic measurement has been demonstrated, which employs equipment that is inexpensive and easy to set up, and which provides output in a convenient form. The method has also been applied to a number of primary and secondary explosives, namely heavy-metal nitrotetrazoles, nitramines, and nitroaromatics. For all primaries and some secondaries thermal explosions were observed, and in all these cases new information regarding the reaction pathway was obtained (Swallowe, Tang, and Krishna Mohan, in press).

Acknowledgments

The authors wish to acknowledge Dr. J. E. Field and Dr. M. M. Chaudhri for useful discussions, Dr. S. Walley for comments on the manuscript, and the Procurement Executive (Ministry of Defence) for financial support.

References

1. T. B. Tang, *Thermochim. Acta* **61**, 341 (1983).
2. V. Krishna Mohan and T. B. Tang, *J. Chem. Phys.* **79** (9), 4271 (1983).
3. Z. Iqbal and A. D. Yoffe, *Proc. Roy. Soc. London Ser. A* **302**, 35 (1967).
4. T. Boddington and Z. Iqbal, *Trans. Faraday Soc.* **65**, 509 (1969).
5. M. E. Brown and G. M. Swallowe, *Thermochim. Acta* **49**, 333 (1981).
6. R. D. Levin and S. G. Lias, "Ionization Potential and Appearance Potential Measurements," Vol. 71, National Standard Reference Data System, National Bureau of Standards (1982).