

Note

Response to the "Discussion" by Johnson and Gallagher

H. PAPAZIAN, P. J. PIZZOLATO AND R. R. ORRELL

Martin Marietta Aerospace, Denver, Colo. 80201 (U. S. A.)

(Received 14 December 1972)

Johnson and Gallagher¹ in their Discussion of our recent work² on the thermal decomposition of aluminum sulfate try to make two main arguments. Their first point is that our thermogravimetric (TG) results are not comparable to isothermal results. Their second point questions our contention that SO is a primary product of decomposition.

As to their first point, they overlook ref. 9 of the work² under discussion where it was shown that TG results on mg samples of silicone polymer give very accurately the activation energy and frequency factor obtained by classical isothermal methods on samples larger by a factor of 500 in both weight and physical dimensions. This type of study was extended³ to several other polymer systems, including heavily filled materials, with equally good results. Further, the activation energy for the thermal decomposition of Teflon by the TG method was compared³ with the independent isothermal study of Madorsky⁴. The value of 82.5 kcal by the TG method compares very favorably with Madorsky's value of 80.5 kcal. These comparative studies on complex polymer systems are certainly a *stringent* test of the TG method and give a high degree of confidence to the results obtained by TG.

It has also been shown³ that unless isothermal decompositions are studied over a wide temperature range one can draw an erroneous conclusion from isothermal studies. For example, the Arrhenius relationship for the thermal decomposition of Dacron by the TG method shows a break in the curve similar to that for aluminum sulfate. Madorsky studied⁴ the isothermal decomposition over a limited temperature range which encompassed the break in the Arrhenius as obtained by TG. He obtained an activation energy of 38 kcal. The TG method yielded two activation energies of 48.3 and 26.5 kcal, the average of which is 37.4 kcal. Thus, unless one is certain that kinetics do not change, an isothermal study over a limited temperature range may lead to error. The temperature range used by Johnson and Gallagher in their isothermal study⁵ of aluminum sulfate encompasses enough of the region where the kinetics are changing to render suspicious their value of 73 kcal for the activation energy. The average of the two energies by the TG method is 62 kcal.

Thus, our experience with both TG and isothermal methods indicates, to us at least, that the TG method has fewer pitfalls than classical isothermal studies of thermal decompositions.

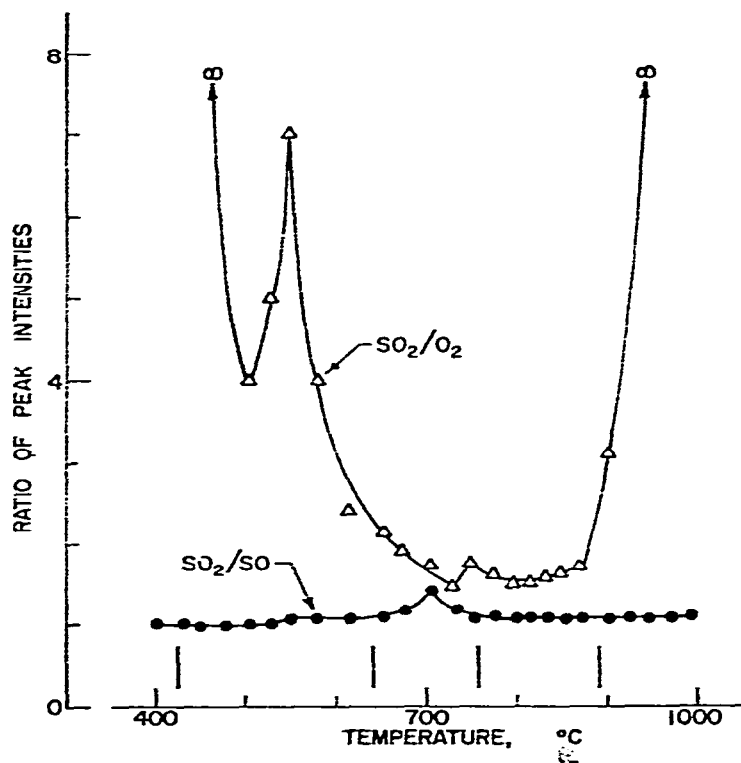


Fig. 1. Ratio of peak intensities as a function of temperature as obtained from the mass spectrometer.

As to their second point questioning SO as a primary product of decomposition of aluminum sulfate, consider Fig. 1. In Fig. 1 are plotted the *ratios* of the peak intensities as obtained (*i.e.*, uncorrected for the various contributions) from the mass spectrometer. It is very difficult, if not impossible, to rationalize these results with the mechanism of decomposition accepted by Johnson and Gallager⁵



If SO^+ resulted from SO_2 then the *ratio* SO_2/SO should be constant with a value 0.49 (as given by the cracking pattern⁶ of SO_2), but as Fig. 1 shows, it is close to 1. If the excess SO^+ results from the cracking of SO_3 in the ionizer of the mass spectrometer then the *ratio* SO_2/SO should vary with temperature as the equilibrium in eqn (2) shifts. Thus, SO must be independent of SO_2 and SO_3 , and in all probability it is a primary product of decomposition.

Furthermore, if eqn (2) is the source of SO_2 and O_2 then the *ratio* SO_2/O_2 should reflect the shift in equilibrium with temperature. As Fig. 1 shows, it does not.

The three vertical lines in the lower part of Fig. 1 delineate temperature regions over which the kinetics change. The two higher temperature regions are those for the two branches of the Arrhenius relationship shown in Fig. 1 of ref. 2. The small peak

in the SO_2/SO ratio reflects the plateau shown in Fig. 2 of ref. 2. The SO_2/O_2 curve is a further indication of the change in kinetics between the two temperature regions. Since the presentation of Fig. 1 here indicates a third change in kinetics as shown by the SO_2/O_2 ratio, we decomposed a much larger sample (50 mg) than studied in ref. 2 and the DTG shows a clear indication of another decomposition region between 435 and 610°C.

Thus, although eqns (1) and (2) may indicate the overall stoichiometry in air, the mechanism of decomposition is considerably different, and in all probability SO is a primary product of decomposition. A careful X-ray diffraction over the entire temperature range appears to be a necessity for an understanding of the thermal decomposition of aluminum sulfate.

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