

SHOCK TUBE-MASS FILTER EXPERIMENTS ON LINEAR TRIATOMIC MOLECULES

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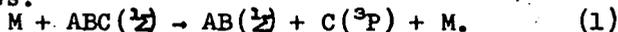
Introduction -- Use of fast mass spectrometry to follow high-temperature gas reactions in a shock tube was first introduced by Bradley and Kistiakowsky (1) and Diesen and Felmler (2) and has been exploited by several groups, all of whom have used a time-of-flight mass spectrometer. We have developed a combination of shock tube and Paul quadrupole mass filter and are using it to study reactions of linear triatomic molecules akin to CO_2 (3-7).

All the mass spectrometric shock sampling techniques have associated with them a number of common problems. These include the uncertainties in temperature caused by our partial ignorance of flow conditions through the sampling orifice into the region of the electron beam and of the rate of gas cooling by thermal transport to the end plate near the sampling leak.

In addition, there are special difficulties, but also special advantages accompanying each particular mass analyzer. The time-of-flight device operates on a cycle in which ionization occurs for only a small fraction of total reaction time (typically about 1/400). This feature limits sensitivity and interferes with noise recognition. However, one gets a full mass spectrum every cycle and can easily survey the species produced in a complex reaction. While a Paul mass filter could be built to operate essentially in the same fashion, it would offer no obvious advantage. It is best suited to the continuous ionization and study of the detailed time behavior of a single mass. Accordingly, mass filter detection is a valuable technique for the study of relatively uncomplicated systems, in which only a few species must be followed. It is also potentially useful for investigating the establishment of flow from the sampling orifice and the approach to steady state conditions in the ion source.

Here I shall outline the principal results of our studies of two related pyrolyses -- NNO and OCS -- and then consider together the existing shock tube data on all molecules of the same family. Of the several stable linear triatomic molecules having the same outer electron structure as that of CO_2 , only four -- CO_2 , N_2O , CS_2 , and OCS -- are common and have been studied under high-temperature shock conditions. Of these, only two -- CO_2 and N_2O -- have been studied extensively, and despite much progress in the past 4 years, there is still disagreement about some details of these decompositions.

Each reactant may be represented $\text{ABC}(\frac{1}{2})$, where C is a calcogen atom and AB is isoelectronic with carbon monoxide. At low pressure, high temperature, and high dilution in an inert gas (M), the first kinetic step is collisional excitation of the internal modes of ABC followed by rapid dissociation of every sufficiently energized reactant as follows:



Under some conditions of temperature and dilution, further steps can occur rapidly. The most important are (2) and (3):



With the mass spectral techniques it is easy to follow all of the possible species -- eg., ABC, C, M, CA, BC, AB, C₂ -- and so determine directly the role of steps such as (2) and (3).

Results -- In the nitrous oxide study (3-5) 4% and 2% mixtures of N₂O in Ar were shocked to temperatures between 1500 and 3500°K. All species found were accounted for by Reactions (1)-(3). All O⁺ signal could be ascribed to fragmentation. Formation of N₂, NO, and O₂ accompanied destruction of N₂O in the proportion of about 3:2:1.⁴ This suggests that Reaction (1) is immediately followed by (2) or (3), with equal probability. The chains and other reactions which we have looked into do not explain the observed distribution of species. That Reactions (2) and (3) keep up with (1) over most of the temperature range indicates that of the various reported expressions for k₂, the most reasonable is that of Fenimore and Jones (8) with an Arrhenius frequency factor of 10¹⁴ cc/mole sec and an activation energy of about 28 kcal. Essentially the same expression would hold for k₃. The general magnitude of these rates has been verified in a number of other shock experiments (9-11). They show an efficient atomic abstraction process with a high activation barrier which implies strong repulsion between triplet-state oxygen atom and N₂O.

Step (1) is of fundamental interest. In order to investigate it, one must know how Reactions (2) and (3) affect the rate. In this case the N₂O starting concentrations were sufficient to insure that the initial rate of N₂O destruction was 2k₁(M)(N₂O) at least up to 2500°K. At much higher dilutions, however, Steps (2) and (3) would be sufficiently slow to be negligible at small reaction times, and the initial rate would be k₁(M)(N₂O). If the experimental activation energy for Step (1) remains much higher than for Steps (2) and (3), at very high temperatures the near steady state concentration of O atom will not pertain, and the rate will drop from 2k₁(M)(N₂O) to k₁(M)(N₂O). It is not certain whether this situation applies in our experiments; therefore, we give the rate expression established for the points below 2500°K: $k_1 = A/\bar{T} (E/RT)^n \exp(-E/RT)$, with $A \approx 1.2 \times 10^7$ cc/mole sec $\sqrt{^\circ K}$, $E = 60$ kcal/mole, $n \approx 5.1$.

In the carbonyl sulfide study (6,7) 4%, 2%, and 0.5% mixtures of OCS in Ar were shocked to temperatures between 2000 and 3200°K. Typical ion current curves are shown in Fig. 1, and results for Step (1) are plotted in Fig. 2. Here the ions OCS⁺, CO⁺, CS⁺, S⁺, O⁺, SO⁺, S₂⁺ were seen. O⁺ is entirely accounted for by fragmentation, but the others are not, except that at low temperatures CS⁺ comes exclusively from fragmentation of OCS. Relative concentrations of S₂ and SO over a temperature range establish that the activation energy for (2) exceeds that for (3) by ca. 19 kcal/mole. In the 0.5% mixtures, the rise of S⁺ signal indicates that a steady state in S is not immediate and establishes the initial rate of OCS disappearance as k₁(M)(OCS). From this, $A \sim 1.1 \times 10^{11}$ cc/mole sec $\sqrt{^\circ K}$, and $n = 1.87$, if E is taken as D₀⁰ = 71.5 kcal/mole. From the quantitative behavior of the S₂⁺, S⁺, and OCS⁺ ion currents, we estimate k₂ $\approx 6 \times 10^{11}$ cc/mole sec at 2600°K. If the steric factor for this reaction is "normal" (0.1 or greater), the activation energy is in the range 20-30 kcal/mole, and there is a barrier to reaction of triplet sulfur atom with OCS that is comparable to the corresponding O + N₂O barrier.

Given the magnitude of k_2 so deduced, one can calculate that at the higher (2% and 4%) percentages of OCS, a near steady-state concentration of S atom would be established almost immediately, and the measured rate would be $2k_1(\text{OCS})(M)$. Although the 2% and 4% measurements were less reliable because of troubles with solid sulfur, which deposited in the sampling orifice, the data indicated a rate about twice that yielded by the 0.5% mixtures, except at the upper end of the temperature range, where the values of k_1 from the 2% mixtures scattered about those from the 0.5% mixtures.

Theory -- The most interesting aspect of the high-temperature study of decomposition of triatomic molecules is the opportunity which it can afford to investigate some consequences of the details of collisional activation. The strong-collision assumption requires that in the steady state all bound quantum states of reactants are populated in Boltzmann fashion, and that the probability of exciting a molecule into an unbound state is proportional to the Boltzmann factor for the final state but independent of initial (bound) state. Thus, to get the reaction rate at low pressures, one need only divide all states into bound and unbound, apply the Boltzmann distribution to all, find the fraction of the Boltzmann population curve which covers unbound states, and multiply by collision rate. Thus, one has an a priori way of predicting reaction rate as a function of temperature (12). The rate should increase somewhat less rapidly with temperature than would be predicted by an Arrhenius extrapolation from low temperature. It is only at very high temperatures that one can expect the difference between the experimental and critical (low-temperature) activation energy to become significant. Thus, accurate data on the temperature dependence of these reaction rates under high-temperature shock conditions are potentially of great fundamental interest.

If the strong-collision assumption is seriously at fault, then reaction may proceed largely by collisional activation of the high-energy bound molecules. This process, in turn, may deplete the populations of the upper bound levels and act to limit the reaction rate. The effect would be expected to increase with temperature and yield a negative contribution to the experimental activation energy.

Accordingly, let us examine pertinent data so far collected on high-temperature activation energies for rupture of molecules of the CO_2 family.

In the case of OCS, the minimum possible critical activation energy is about 71.5 kcal/mole, the over-all dissociation energy D_0° . Our observed activation energy (7) over the range 1950-3150°K is 64.5 kcal/mole. Since at 2550°K the vibrational system of OCS is already excited by 15.5 kcal/mole and as the collision frequency involves an effective activation energy of $(1/2)RT = 2.5$ kcal/mole, the minimum expected over-all activation energy would be $71.5 - 13 = 58.5$ kcal/mole. On the basis of any strong-collision theory, which states that active molecules are formed in a Boltzmann distribution, about $1.2RT = 6$ kcal/mole is stored in vibrations of the average active molecule formed, putting the expected minimum experimental activation energy at 64.5 kcal/mole ($=58.5+6$), in agreement with that observed. Therefore, according to our current knowledge of the parameters involved in the OCS dissociation, the strong-collision

theory (such as the RRKM treatment) is not in conflict with the experiment. However, we lack independent information about the critical activation energy (which could be higher than the dissociation energy, as is apparently the case in N_2O (5)) or the activated complex (bottleneck) configuration (which tells us how to treat rotations in the strong-collision approach (7,12)). Therefore, predictions based on the strong-collision theory may not be shown to agree with the facts. Indeed, our calculations based on the RRKM theory (7) show that a low (~1%) collisional activation efficiency λ_D is required to fit the observed rates, and this may be considered reasonable grounds for suspecting the strong-collision model, as certainly not 99 of every 100 collisions are elastic. To make λ_D larger, one has to assume a larger critical activation energy, which in turn means that the experimental activation energy shows a negative term not provided by the strong-collision treatment.

In the case of SCS, the critical activation energy is sure to be essentially the dissociation energy, $D_0^0 = 96$ kcal/mole for $SCS(^1\Sigma) \rightarrow CS(^1\Sigma) + S(^3P)$; the reaction proceeds through the bent 3A_2 state of CS_2 , which is stable. The experimental activation energy has been reported (13) as 80.3 kcal/mole over the range 1800 to 3700°K. At 2850°K, 18.3 kcal/mole is stored in the vibrational modes of OCS, and correction for the temperature dependence of collision frequency brings the possible minimum expected activation energy to about $96. + 2.8 - 18.3 = 80.5$ kcal/mole. The strong-collision approximation adds about 6.5 kcal to this, bringing the expected strong-collision activation energy to about 87 kcal/mole. It is possible that a rotational correction is required (7,12), which might reduce this by as much as 2 kcal/mole; regardless, there is a discrepancy indicating the effective activation energy to be a bit too small to be explained within the strong-collision framework.

The large number of shock tube studies on N_2O rupture include at least one employing an infrared detection technique (14), two involving ultraviolet absorption measurements (11,14), three employing time-of-flight mass spectrometry, and ours using the quadrupole mass filter. The various investigators report experimental activation energies ranging from 30 to 49 kcal/mole, except for one study (11) which yielded 58 kcal/mole. There appears to be an activation barrier to recombination, giving a critical activation energy in the vicinity of 60 kcal/mole for $N_2O(^1\Sigma) \rightarrow N_2(^1\Sigma) + O(^3P)$. At the mean temperature of most of the experiments (~2250°K), there is roughly 12.5 kcal vibrational excitation; $60 - 12.5 + 2.2 \approx 50$ kcal/mole. With active molecules being formed with about 5 kcal average excess energy, in the strong-collision model we might expect an activation energy of about 55 kcal/mole; rotation would decrease it by 1-2 kcal (7). Fig. 3 shows data from various studies fitted to a least-squares Arrhenius line. It would be hard to reconcile the experiments with the strong-collision result. The discrepancy in activation energy is about $4RT$. The apparent collisional activation efficiency also is very small.

Several shock studies of OCO decomposition are on record; all have been done by spectroscopic techniques. The experimental activation energies from several of the studies are as follows:

Reference	T	$E_{\text{exp}} - \frac{1}{2} RT$	E_a (s.c.)	$D_0^0 - E_a$ (s.c.) $\langle RT \rangle$
(15)	2500-3000°K	86 kcal	95	5.5
(16)	2850-4200	95.5	110	2.2
(17)	3000-5000	84.5	99	3.2
(18)	3500-6000	74.5	92	3.7
(19)	6000-11000	62	93	2.1

Here, E_{exp} denotes experimental activation energy ($-\frac{d \ln k}{d(1/RT)}$) and E_a (s.c.) denotes the critical activation energy which, on a strong-collision model, would be computible with the given E_{exp} . Notice that the highest experimental activation energy obtained is still 30 kcal below the minimum dissociation energy, 126 kcal/mole.

In general, the preponderance of kinetic information so far obtained with shock experiments on low-pressure dissociations of linear triatomic molecules at high temperatures indicates a smaller temperature coefficient of rate than is predicted by the strong-collision theory of vibrational activation. However, more precise experimentation should be done. The effect is evidence of either some fairly widespread systematic error in shock measurements (such as a temperature error) or some serious breakdown of the (strong collision) theory.

Recently, Tardy and Rabinovitch(20) have reported a series of calculations on various stochastic weak-collision models for excitation. They found that the strong-collision rate expression requires a correction factor, β , which proved to be fairly insensitive to the details of the particular model chosen and principally dependent on $\langle \Delta E \rangle / \langle E^+ \rangle$, where $\langle \Delta E \rangle$ denotes the average energy transferred per down collision and $\langle E^+ \rangle$ denotes the mean energy of the active molecules in the strong-collision model. Ignoring any dependence of $\langle \Delta E \rangle$ on temperature, we find that for β between 0.2 and 0.01, $-\frac{d \ln \beta}{d(1/RT)} < -2 RT$. There is thus some theoretical justification for blaming an abnormally large high-temperature falloff of experimental activation energy on a weak-collisional energy transfer process.

Conclusion -- Measurements of temperature dependence in the rates of unimolecular reactions of small molecules in the second-order (low pressure) region offer exciting and heretofore unexploited opportunities to investigate certain aspects of the collisional activation process. However, precise data and particularly reliable temperature measurements are necessary. The considerable disagreement among various laboratories in the case of the reactions discussed here is prima facie evidence that accuracy sufficient to the purpose has not been routinely attained by most shock tube groups. Nevertheless, there is a general pattern of anomalously low activation energies at very high temperatures which suggests a weak-collision process with reactive depletion of the upper bound levels.

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Figures

- Fig. 1a Sample, experimental oscilloscope traces of ion currents from shocks, OCS 0.5% in Ar, $\sim 2800^\circ\text{K}$. A: OCS^+ . B: CO^+ . C: S^+ . D: S_2^+ . E: CS^+ . F: SO^+ . The smooth line is a signal from a thin-film resistor in the shock tube end wall. Fine marks appear on the bottom line, 200 μsec . apart.
- Fig. 1b Typical adjustment of S^+ , CS^+ , and CO^+ dynamic in current curves to correct for OCS fragmentation.
- Fig. 2 Second-order rate constants (k_1) for the disappearance of OCS, 0.5% in Ar. Open circles correspond to initial pressure of 6 ton; shaded ones, 8 ton. The line is the result of a quantum RRKM calculation for an assumed critical activation energy of 71.5 kcal/mole, and $\lambda_D \approx 0.01$.
- Fig. 3 Arrhenius plot of second-order rate constants ($2k_1$) disappearance of N_2O , 1-4% in Ar. +: Our data. Other symbols denote other laboratories. Solid line: $k = 10^{12.4} \exp(-35.4 \text{ kcal/RT mole})$, from least-squares fit with half-weighting of our data. Dotted line: with equal weighting of all data.

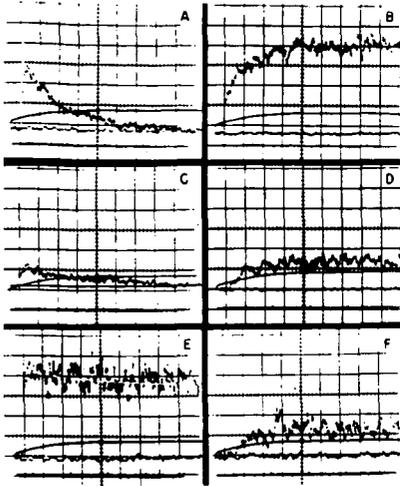


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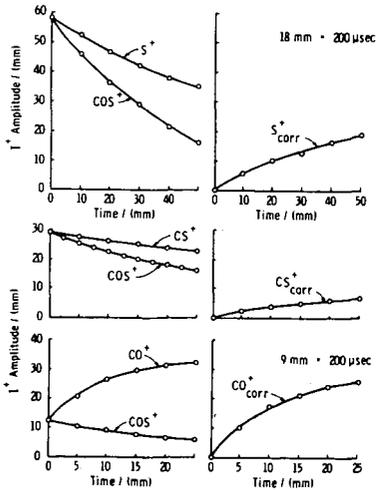


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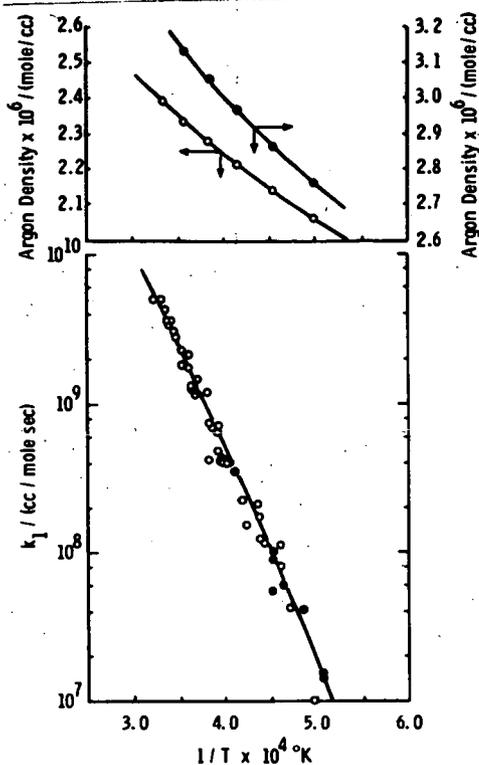


Fig. 2. Second-order rate constants (k_1) for the disappearance of OCS, 0.5% in Ar. Open circles correspond to initial pressure of 6 torr; shaded ones, 8 torr. The line is the result of a quantum RRKM calculations for an assumed critical activation energy of 71.5 kcal/mole, and $\lambda_D \approx 0.01$

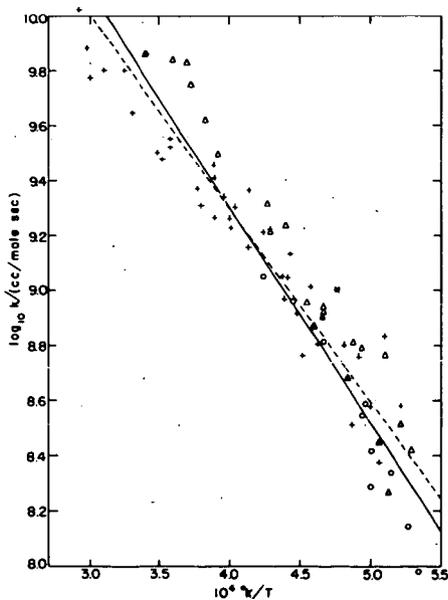


Fig. 3. Arrhenius plot of second-order rate constants for ($2k_1$) disappearance of N_2O , 1-4% in Ar. +: Our data. Other symbols denote other laboratories. Solid line: $k = 10^{12.4} \exp(-35.4 \text{ kcal/RT mole})$, from least-squares fit with half-weighting of our data. Dotted line: with equal weighting of all data.