Evidence for a New Intermediate in N_2O_5 Decomposition

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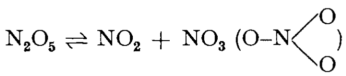
Summary CO_2 is formed in small yields in the gas-phase reaction of N_2O_5 and CO mixtures and the variation with composition precludes the source being the reaction of CO with the known intermediates in N_2O_5 decomposition; a peroxy-NO_3 radical is proposed as the new intermediate with the critical role.

The accepted mechanism of N_2O_5 gas thermal decomposition[1] involves the steps in reactions (1)—(3). The establishment



$$N_2O_5 \rightleftharpoons NO_2 + NO_3\ (O\text{–}N\langle^{O}_{O}) \quad (1)$$

$$NO_2 + NO_3 \rightarrow NO + O_2 + NO_2 \quad (2)$$

$$NO + NO_3/N_2O_5 \rightarrow NO_2 + NO_2/2NO_2 \quad (3)$$

of the initial pre-equilibrium has been shown by ^{14}N, ^{15}N isotopic scrambling experiments.[2] Upon addition of CO, the only feasible source of CO_2 on the basis of this mechanism would be reaction (4) which has been postulated before.[3,4]

$$NO_3 + CO \rightarrow NO_2 + CO_2 \quad (4)$$

We have found that CO_2 is formed in small yields in the thermal decomposition of N_2O_5 vapour in the presence of CO in a static reactor in the temperature range 291–343 K. N_2O_5 was synthesized immediately prior to use by the method of Caesar and Goldfrank[5] and was obtained as a pure white solid at *ca.* 253 K, which was extensively pumped to remove residual NO_2. The vapour was distilled into the Pyrex glass reactor (internal volume 0·20 dm^3) to a pressure in the range 0·4—7·0 kPa and was then frozen at *ca.* 253 K. Carbon monoxide (B.O.C. technical grade) was purified as described previously[6] and was injected into the reactor to a pressure of 40—60 kPa above the frozen N_2O_5. Following isolation, the reactor was immersed in a water bath maintained at the required temperature and the decomposition of N_2O_5 was allowed to go to completion on the basis of established rate data for this process.[7] Subsequently CO_2 yields were analysed by the gas chromatographic procedures described before.[8]

In a set of experiments at 313 K, it was found that the ratio (r) of the final partial pressure of CO_2 in the reactor to the partial pressure of CO was $(2{\cdot}0 \pm 0{\cdot}3) \times 10^{-4}$, independent of the initial partial pressure of N_2O_5 in the ranges given above. Also when up to 7 kPa of NO_2 was added to the initial reaction mixture, the value of r was not decreased, a point verified also at 332 K. At 293 K, when a reaction time of *ca.* 70 h was required to ensure essentially complete decomposition of N_2O_5, the CO_2 yield was found to rise steadily towards the limiting value throughout the decomposition, rather than only in its early stages. Further the value of r decreased with increasing temperature; a plot of $\ln r$ *vs.* T^{-1} had a slope which corresponded to an apparent activation energy of -30 ± 5 kJ mol^{-1}.

Reaction (4) cannot be a significant source of CO_2 in our experiments. If this were the case, then direct competition between NO_2 and CO for NO_3 in reactions (2) and (4) would have made r depend inversely on $[NO_2]$; since NO_2 is a final product of the decomposition of N_2O_5, the major part of CO_2 formation should have been restricted to the early stages when $[NO_2]$ is low. Moreover r is predicted to decrease with decreasing initial $[N_2O_5]$. None of these predictions agrees with the observations.

In order to explain our results, it is necessary that an oxidizing species other than the symmetric NO_3 of the original mechanism is formed. A possible candidate comes from Siddall's suggestion[4] that reaction (2) is unlikely to proceed as a single elementary step and the mechanism involves the formation of the peroxy-NO_3 species (ONOO) as intermediate by the O-atom transfer step (5).

$$NO_2 + NO_3 \rightarrow NO_2 + ONOO \quad (5)$$

This asymmetric ONOO species was proposed originally by Ogg[9] on the basis of isotope exchange experiments for O_2 and NO_2 in the presence of NO. We consider it to be the most likely identity of the oxidizing species required to interpret our results on the basis that it reacts in a minor removal step (6) to form CO_2, while its predominant removal step is

$$ONOO + CO \rightarrow NO_2 + CO_2 \quad (6)$$

reaction with N_2O_5 in a necessarily complex process represented by reaction (7). The key requirement of our mechan-

$$ONOO + N_2O_5 \rightarrow \text{Products} \rightarrow 3NO_2 + O_2 \quad (7)$$

ism is that ONOO does not react at a significant rate with NO_2. In this event the continuing formation of CO_2 throughout the decomposition reaction can be explained and the addition of NO_2 initially should not affect r. Also as the initial $[N_2O_5]$ decreases, compensation occurs between the decreased integrated formation rate of ONOO and the increased proportion of ONOO which reacts in step (6), so that r can be independent of the initial $[N_2O_5]$. However it should be pointed out that our small yields of CO_2 do not require that reaction (5) constitutes more than a small part of reaction (2), if the latter is to be regarded as a proper component of the overall mechanism.

The negative apparent activation energy (E_a) of r is too large for an explanation to be sought in a complex-formation mechanism and it must therefore arise from a combination of the activation energies (E) attaching to the rate constants of the elementary steps. On the simplest basis, we can take Siddall's proposal[4] as implying that reaction (5) is the rate-determining step of the reaction represented by equation (2) and hence E_2 and E_5 will be the same with the consequence that $E_a = E_6 - E_7 = -30 \pm 5$ kJ mol^{-1}. This demands that the minor reaction (6) has a low Arrhenius pre-exponential factor in combination with a low value of E_6 in order to satisfy the requirement that the predominant reaction of ONOO radicals in reaction (7) cannot be the rate-determining step of the overall N_2O_5 decomposition on the basis of the established first-order kinetics, *i.e.* E_7 appears unlikely to be much in excess of 30 kJ mol^{-1}.

Some heterogeneous mechanism occurring on the walls of the reaction vessel is also possible. However N_2O_5 decomposition has always been regarded as a homogeneous reaction and the relatively high total pressures used in this work would inhibit diffusion of species to the walls. The negative E_a attaching to r would be difficult to explain on this basis. Thus this appears to be a less likely possibility.

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