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Final Report

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Title: The Molecular Dynamics of Atmospheric Reaction

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Short Abstract:

The purpose of this research was to obtain detailed information concerning the molecular mechanics (the 'dynamics') of reactions which play a part in the chemistry of the upper atmosphere. The detailed information took the form of quantitative data concerning the rate of reaction into specified states of <u>product</u> vibration, rotation and translation ($k(v',J',T')$) for exothermic reaction, and hence similar information concerning the rate of reaction from specified states of <u>reagent</u> vibration, rotation and translation ($k(v',J',T')$) for endothermic reaction. The techniques used were variants on the infrared chemiluminescence method, developed over the past decade in the principal investigator's laboratory. The method is, at the present time, the only one that provides data at this level of detail. Particular emphasis was placed initially on reactions that formed, and that removed, vibrationally-excited hydroxyl radicals. Fundamental studies were also performed on exothermic (and hence endothermic) reactions involving hydrogen halides -- the non-equilibrium chemistry of these species could be of great importance in the upper atmosphere.

Final Report

Current chemical research is beginning to reveal the nature of the atomic and molecular motions during the course of a chemical reaction. If we are to understand the behavior of a reacting system, it is vital that we know not only the gross rate of reaction, but what might be termed the 'fine structure' of that rate. By this is meant the dependence of the rate on the partitioning of the reagent energy between vibration, rotation and translation (and in some cases electronic excitation) in the reagents and products. This is particularly important in reactive systems at low pressures, where reagents and products often exist in states of thermal disequilibrium. The upper atmosphere is just such a system [1].

There exist today two techniques which can be applied to the determination of the detailed dynamics of simple chemical reactions. One of these is the method of crossed molecular beams [2]. This method gives details concerning the translational energy in the reaction-products (and hence the sum of the vibrational and rotational excitation, which constitutes the balance of the energy), and concerning the angular distribution in the products. The other method gives detailed information regarding the vibrational, rotational, and (hence) translational, energy-distributions in the products of exothermic reactions. By application of microscopic reversibility it is possible to derive similarly detailed information concerning the effect on the rate of the reverse (endothermic) reactions, of variation in the distribution of the reagent energy among vibration, rotation and translation [5,6].

The infrared chemiluminescence method has been applied under this Grant principally to the reactions (i) $H + O_3 \rightarrow OH + O_2$ [N1,N2] (the references preceded by a letter N can be found in the list of "Papers Published with the Support of NASA Grant NGR 52-026-028), (ii) $H + Cl_2 \rightarrow HCl + Cl$ [N3,N13], (iii) $H + SCl_2 \rightarrow HCl + SCl$ [N4], (iv) $Cl + HI \rightarrow HCl + I$ [N7,N12], (v) $H + F_2 \rightarrow HF + F$ [N14], (vi) $F + HCl \rightarrow HF + Cl$ [N17]. These experimental studies have been supplemented by theoretical studies applying the classical trajectory method (in 3D) [N6,N15] or simple analytical considerations [N8,N18]. Some work was performed on the peripheral topics of electronic-to-vibrational energy-transfer, and rotational-to-translational energy transfer. The details of both of these processes have relevance to the energy distributions of reacting species in the upper atmosphere.

The main findings from this work can be summarised as follows:

(1) The two variants of the infrared chemiluminescence method termed 'measured relaxation (M.R.)' and 'arrested relaxation (A.R.)' give initial vibrational distributions in reaction products, $k(v')$, that are in satisfactory agreement [Paper N3 and N13].

(2) The reaction $H + O_3 \rightarrow OH(v',J') + O_2$ channels its exothermicity into vibrational and rotational excitation of OH, with extremely high efficiency. The potential-energy surface must be highly 'attractive', for a reaction of

atomic H to show these dynamics. The vibrational excitation of the second reaction product, O_2, is negligible [Paper N2].

(3) The reaction H + $SCl_2 \rightarrow HCl + SCl$ showed evidence of two types of reaction dynamics, i.e. two characteristic paths across the potential-energy hypersurface led to the same reaction products with different vibrational-rotational energy distributions. This intriguing finding was, however, not conclusive. A further study is planned [Paper N4].

(4) Electronic-to-vibrational energy transfer (in Hg* + HF) was an efficient process despite being non-resonant. Progressively higher vibrational levels were populated with diminishing efficiency; i.e. k(v) fell rapidly with increase in v up to the limit of detection, v=6. [Paper N5].

(5) Reactions proceeding across potential-energy hypersurfaces which (viewed on the collinear section through the hypersurface) have an early barrier-crest, proceed most rapidly if the reagent energy is vested in relative translation. (The reaction $H + O_3 \rightarrow OH + O_2$ would be of this type since an exothermic reaction has an early barrier, particularly if the surface is 'attractive'). Reagent vibration (for example in an O_3 stretching mode) would be less effective in promoting the reaction. The effect on the dynamics of a light attacking atom (as in $H + O_3$) was shown to be such as to diminish but not to remove this 'preference' for reagent translation. For surfaces with a late barrier-crest

(for example the endothermic reaction $OH + O_2 \rightarrow H + O_3$) vibration would be by far the most effective form of reagent-energy for promoting reaction. [Paper N6].

(6) Under this grant a method was developed for semi-quantitative studies of the effect of changing reagent energy on product energy-distribution. Atomic H formed by vacuum u.v. photolysis in the upper atmosphere would have a greatly enhanced translational energy and consequently would react with high probability with O_3 (see (5) above). This could distort the product vibrational energy distribution. Alternatively the absorption of light, or energy-transfer processes, could give rise to vibrationally-excited O_3 which would also react with atomic H to produce a modified $OH(v',J')$ product-distribution. Experimental studies, and theoretical studies also, have led us to conclude that reagent translational energy, ΔT, in excess of the barrier to reaction is converted predominantly into product translation and rotation, $\Delta T' + \Delta R'$. By contrast reagent vibration, ΔV, becomes product vibration, $\Delta V'$. [The beginnings of these studies are to be found in papers N7 and N17 both of which are experimental, and in the theoretical study, N15].

(7) Exothermic chemical reactions frequently give rise to reaction products in a fairly narrow range of highly rotationally-excited states. At the pressures that apply in the upper atmosphere a molecule will suffer $\sim 10\text{-}10^3$ collisions before reacting, or radiating in the infrared. There is evidence that this number of collisions is insufficient to produce complete rotational thermalisation in molecules of

low moment-of-inertia (such as OH). It is therefore of interest to examine the pattern of rotational relaxation. This was done experimentally, with interesting results. The peculiar double-peaked rotational distribution that was found to be produced by the relaxation could be explained by a simple model according to which the probability of rotational-to-translational energy-transfer diminished exponentially with increasing energy of the rotational quantum being transferred. [Paper N8].

(8) Mention has been made (under items (2), (3) and (5), for example) of the importance of the 'geography' of the 'potential-energy hypersurface' -- that incorporates information regarding the interatomic forces -- in determining the particulars of the reaction dynamics. It is of interest to know whether purely 'kinematic' effects deriving from the relative masses of the reacting species can predominate In experimental and theoretical studies of the reactions $X + HY \rightarrow HX + Y$ (where X and Y were halogen atoms), $X + H_2 \rightarrow XH + H$, and $H + X_2 \rightarrow HX + X$, we have found good evidence for a large 'kinematic' effect. Briefly-stated this effect derives from the slow approach of the heavy attacking atom in $X + HY$ and $X + H_2$ (the approach is slow for $X + H_2$ compared with the rapid separation of the atoms in H_2), and the rapid approach of the light attacking atom in $H + X_2$ (or $H + O_3$). One consequence is an efficient conversion of reaction energy into internal excitation of the new molecule in the former case (even on a 'repulsive' energy-surface), and a much lower efficiency in the latter

case (on a 'repulsive' energy-surface). [Papers N12, N13, N14, N15, N18].

(9) In a speculative review-article attention was drawn to the possible importance of anisotropy in scattering angles, and of translational (and perhaps rotational) disequilibrium, in the products of reactions occurring in interstellar space. [Paper N11].

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