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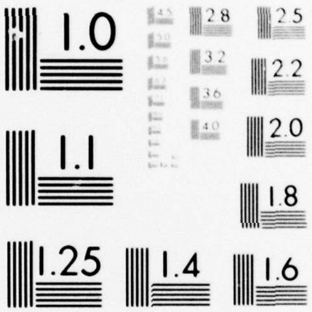

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It has been shown that for the prototype system K+HCl = KCl + H, one quantum of vibrational excitation accelerates the reaction about two orders of magnitude, and that translational energy is only about 10 percent as effective as a comparable amount of vibrational energy. The input of an excess of translational energy is shown to decrease the reaction probability. The state-to-state rate constant is found to vary exponentially with $-(E')^{1/2}$, where E' is the translational energy in excess of the thermodynamic requirement.

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"INELASTIC AND REACTIVE COLLISIONS OF TRANSLATIONALLY EXCITED MOLECULES"

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INELASTIC AND REACTIVE SCATTERING OF TRANSLATIONALLY EXCITED MOLECULES

FINAL REPORT

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The time-honored method of increasing the rate of a chemical reaction is to raise the temperature of the reagents. In almost every case studied, the rate is found to depend exponentially with temperature in the form first discovered by Arrhenius $R \propto \exp(-E_a/RT)$. This form is so common that the exponential constant E_a, called the "activation energy," is considered to be half the goal of a kinetic investigation, the other half being the pre-exponential, or frequency factor. The "activation energy," E_a, is regarded as the critical energy which must be supplied to a colliding pair in order to induce reaction. This interpretation is convenient, but one must remember that E_a is strictly an empirical parameter, and theoretical interpretation is not complete. This research was undertaken to investigate the nature of the activation energy: What is it? Why must it be overcome? How must it be supplied? The answers to questions such as these would not only be of importance to theory, but would also be of practical importance in characterizing various non-equilibrium systems in shock waves, discharges, lasers, etc.

Our attention has been focussed upon the last question: how can a chemical system be activated? To answer this question we have initiated a program to investigate the effectiveness of energy contained in the various internal degrees of freedom of a bimolecular collision, translation [T], vibration [V], rotation [R], and electronic [E]. The collisions are studied in the intersection of two molecular beams where all modes are not populated according to equilibrium Boltzmann statistics representing a single temperature since a zero-order experiment could be done with each beam emanating from a separate oven so that two temperatures would have to be used to characterize the system. The collision free properties of molecular beams actually allow us to go even farther than this however: we can velocity monochromate a beam, and for a small class of molecules we can use lasers to selectively excite different internal states of atoms and molecules. In this way we are able to study the separate effects of [T] and [V] on chemical reactivity.

The K + HCl → KCl + H system was chosen as a prototype reaction because a) it appeared to have a small (2 kcal/mole) activation energy which could easily be supplied even from a hot oven, and b) a resonant chemical laser (HCl) was available to excite the molecule. Early experiments showed that one quantum of [V], 8.3 kcal/mole, added to a molecule without changing its speed increased the reactive cross section ∿ 100X over the ground state. In the complementary experiment we changed [T] without changing [V] and showed that a similar amount of energy (up to 12 kcal/mole) increased the cross section by only a modest amount, ∿ 10X. We have more recently increased the speed of the reagents to ∿ 23 kcal/mole [1 eV or ∿ 11,000°K] and observed that the cross section decreases at energies above ∿ 12 kcal/mole.

The mere observation of a change in cross section suffices initially, but in the long range one hopes to correlate similar results on other systems, to understand how molecular structure affects these results, and to predict the behavior of yet unstudied systems. In an attempt to progress in this direction we considered the role played by the conservation laws regarding the variation of the cross section with energy. It became apparent that as the initial energy were changed, a different set of product states would evolve from the reaction. A measurement of rate variation with energy therefore contains information on a) how the final states change with energy (a purely statistical effect) and b) how the rate constant for forming a single product state changes with energy (the dynamical effect of interest). The experimental rate constant, k, is $k = \bar{\omega}\rho$, where ρ is the density of possible product states of the isolated products.

Spectroscopic data can be used to calculate the density of product states, ρ, at various energies, so the dynamically interesting $\bar{\omega}$ can be extracted from the experimental data. Note that this formulation correctly accounts for the threshold region: if the reaction cannot occur, no product states are possible, ρ is zero and therefore so is k. When our data for the energy dependence of the K + HCl reaction is analyzed in this way, we find that $\bar{\omega}$ varies with translational energy as $\exp[-\beta(E')^{1/2}]$ where E' is the translational energy in excess of the thermodynamic requirement. This energy dependence is not yet understood, but could prove enormously useful if found to be applicable to other systems. For example, we predicted the decrease in experimental rate constant in the 12-20 kcal/mole range by extrapolating the exponential decrease of $\bar{\omega}$ into this region. Note that while this formulation is the proper way to interpret experimental data [regardless of the mathematical form of the results], we must apply it to reactions which are exothermic. Endothermic bimolecular reactions do not occur. They appear to occur in Boltzmann systems because molecules in the high energy "tails" have enough energy that their collisions are exo. An increase in energy for such a Boltzmann system will thus change $\bar{\omega}$, increase ρ, and most importantly, will increase (exponentially) the fraction which can react. Claims of enormous enhancement in bimolecular reaction rates upon irradiation with IR lasers for endothermic reactions in Boltzmann equilibrium are consequently not surprising — irradiation just increases the fraction of collisions which are exothermic.

Considerable effort was put into the construction and testing of the apparatus necessary to perform these experiments. We designed (after plans from Professor J. C. Polanyi and Professor T. A. Cool) and built a CW chemical laser, and we are now able to get about 2 watts of CW emission in the HCl $V = 1 \rightarrow 0$ fundamental, roughly equally distributed over P(3)-P(6). Within the last month we have been able to obtain reactive scattering angular distributions for vibrationally excited HCl. Our ability to take and interpret data has been remarkably enhanced by interfacing a computer to the molecular beam machine.

Finally, we note that we have just begun a study to investigate the effect of electronic energy on a chemical reaction. The excited (by 121 cm^{-1}) $^2\Pi_{3/2}$ state of NO has been reported to be much more reactive towards O_3 than the ground $^2\Pi_{1/2}$ state. We have built a beam apparatus to state select the $^2\Pi_{3/2}$ level of a NO beam using the deflection obtained in an inhomogeneous magnetic field. The apparatus is currently being tested, although some inconclusive experiments have been performed.

In summary, we have

1) Shown that for the prototype system $K + HCl \rightarrow KCl + H$ vibrational excitation accelerates the reaction about two orders of magnitude. Recent experiments show this enhancement is due to absorption of only one photon.
2) Shown that translational energy is only about 10% as effective as a comparable amount of vibrational energy.
3) Shown that even more translational energy than one quantum of vibration decreases reaction probability.

4) Shown how to compare these effects for different reactions by extracting the average state-to-state cross section from the experimental results.

5) Designed and constructed a CW chemical laser, a molecular beam apparatus for studying the electronic state-selected reaction $NO + O_3 \rightarrow NO_2 + O_2$, and interfaced a computer to the molecular beam apparatus used to study translational/vibrational energy effects on reactivity. We are now poised to extend these studies to other chemical systems to broaden our understanding of the consumption of energy in chemical reactions.

PUBLICATIONS

"Translational Excitation of the Molecular Beam Reaction $K + HCl \rightarrow KCl + H$," J. Gary Pruett, Frederick R. Grabiner and Philip R. Brooks, J. Chem. Phys., 63, 1173 (1975).

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