the function of dioldehydratases.

While the present study has involved organocobalt substrates, the general features are expected to be characteristic of photohomolysis in most transition metal complexes. More specifically, we can anticipate that, in those systems for which ϕ_R is a constant (significantly less than unity) over an appreciable range of excitation energies greater than E_{th}, there will be considerable excited-state thermalization and numerical values of ϕ_R will be a function of both excited-state dynamics and radical pair recombination statistics.

References and Notes

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Flow Tube Measurement of the Rate Constants of the $N(^2D, ^2P, \text{and } ^4S) + Cl_2$ Reactions

Sir:

Love et al.[1] have recently published the first results of their crossed molecular beam experiments of atomic nitrogen plus halogen reactions. Their arc-heated (7000–15 000 K) nozzle beam source produces a mixture of $N(^4S, ^2D, \text{and } ^2P)$ species, which complicates the analysis of their reactive scattering data.

We present here the results of a brief kinetic study, at 298 K, of the $N(^2D) + Cl_2$, $N(^2P) + Cl_2$, and ground-state $N(^4S) + Cl_2$ reactions using the discharge-flow, resonance fluorescence method. The metastables are found to react very rapidly with Cl_2, i.e., $k_{^2D} = 3.6 \times 10^{-11}$ and $k_{^2P} = 2.2 \times 10^{-11}$ cm^3 s^{-1}. Their high detectability ($\gtrsim 10^9$ cm^{-3}) and low initial concentration ($\sim 10^{11-12}$ cm^{-3}) permits the unambiguous measurement of elementary rate constants. The reaction of ground-state N atoms is about four orders of magnitude slower, $k_{^4S} \simeq 2 \times 10^{-15}$ cm^3 s^{-1}, and, although this value is in qualitative agreement with two published results,[2,3] it lies near the lower limit of the measurable range accessible to this method.

The flow tube apparatus is a modification of an earlier one,[4] the principal difference being the use of resonance fluorescence rather than absorption which increases detection sensitivity by a factor of 10. This makes it possible to measure the kinetics of $N(^2P)$ whose initial concentration is smaller than that of $N(^2D)$ by about a factor of 6. A microwave discharge in flowing He + 1% N_2, which emits the strong multiplets at

149.2 (^2D) and 174.2 nm (^2P), serves as the resonance lamp. Since both transitions have a common upper state, one or the other multiplet must be isolated in a given experiment; i.e., for $N(^2P)$ detection, a Suprasil-2 quartz window passes 174.2- but blocks 149.2-nm radiation, and for $N(^2D)$ a band rejection filter (Acton Research Corp.) passes only 149.2-nm radiation. Since the fluorescence is emitted at both multiplets, the signal is monitored at a wavelength other than that used to excite the fluorescence with a resultant improvement in scattered light suppression. A 0.5-m vacuum monochromator (Jarrell-Ash, Model 84-110) and solar blind photomultiplier (EMR, Model 541-GX) are used to measure the resonance absorption or fluorescence signals at the downstream end of the 2.5-cm i.d. flow tube. Absorption of radiation by Cl_2 at 149.2 and 174.2 nm was found to be negligible over the range of concentrations used.

Atomic species are produced in a microwave discharge 26 cm upstream of the fluorescence cell in flowing Ar (~3 Torr) containing ~1% N_2. Cl_2 ($\leq 1\%$ in Ar) is added 14 cm upstream of the cell through a multiperforated, fast-mixing glass loop. Typical Cl_2 concentrations range from 8 to 80×10^{12} cm^{-3} for the fast metastable reactions and from 1 to 25×10^{14} for the slow $N(^4S)$ reaction. Reaction times are 4.5 ms for the metastable and 50 ms for the ground-state reaction. Earlier experiments in which the discharge atom source was moved had shown that metastables are efficiently removed by surface deactivation whereas $N(^4S)$ persists with negligible loss. For the metastable reactions it is important to know whether laminar flow is established in the reaction region,[5] since fully laminar flow introduces a factor of 1.6 by which the "plug-flow" rate constant must be multiplied for species whose concentration near the surface is zero. Our flow conditions are intermediate between plug- and laminar flow for M = Ar, whereas for M = He they are calculated to be purely laminar.[5] This was confirmed by studies of $N(^2D$ and $^2P)$ with O_2 which gave consistent k's when factors of 1.3 and 1.6 were used for M = Ar and He, respectively. The metastable + Cl_2 rate constants reported here use the factor 1.3, but, since its total range is 1.0 to 1.6, a maximum error of 30% may be incurred.

Accurately linear plots of ln I_F vs. $[Cl_2]$ (I_F = resonance fluorescence signal) for six series of experiments, each consisting of five to six different Cl_2 additions, gave $k_{2D} = (3.60 \pm 0.4) \times 10^{-11}$ cm^3 s^{-1}, where the k's are the slopes multiplied by 1.3 and divided by the average reaction time, t. The individual experiments gave rate constants of 3.53, 4.19, 3.17, 3.68, 3.42, and 3.36×10^{-11} cm^3 s^{-1} with correlation coefficients of 0.970 to 0.998 for the least-squares fits of the linear ln I_F vs. $[Cl_2]$ plots. Similar experiments for $N(^2P)$ gave $k_{2P} = 2.16 \pm 0.2 \times 10^{-11}$ cm^3 s^{-1} from individual values of 2.08, 2.12, 2.39, and 2.05×10^{-11} cm^3 s^{-1} with correlation coefficients of 0.990 to 0.998.

For the very much slower $N(^4S)$ reaction, $[N(^4S)]$ was monitored by the intensity of the (11, 7) band of the first positive system ($B^3\Pi - A^3\Sigma_u^+$) of N_2 whose intensity is known to be proportional to $[N]^2$ under these conditions.[6] It was also assumed that the reaction product, NCl, reacts rapidly with excess $N(^4S)$ so that k_{4S} is given by $1/4t$ times the slope of the semilog plot of intensity vs. $[Cl_2]$. Because of the low flow velocity in these experiments, the N-metastable concentrations will have decayed to negligibly small values before Cl_2 is added to the flow. Three $N(^4S)$ experiments gave $k_{4S} = 2 \times 10^{-15}$ cm^3 s^{-1}. This is likely to be an upper limit, since our brief investigation did not fully eliminate small changes in the surface properties of the flow tube that may contribute to the slow observed decay.

It has been shown[7] that a small amount of $N(^2P)$ is produced from $N(^4S)$ in the nitrogen afterglow, presumably by reaction of $N(^4S)$ with $N_2(A^3\Sigma_u^+)$. The corresponding $[N(^2P)]$ should therefore be proportional to $[N(^4S)]^2$, and relatively constant as a consequence of the slow decay of $N(^4S)$. This steady-state $[N(^2P)]$ is much smaller than that formed in the discharge source as evidenced by the measured linear semilog decay of $[N(^2P)]$, without showing any leveling off, when the discharge source was moved along the flow tube.

Whether the observed removal of $N(^2D$ or $^2P)$ by Cl_2 is due to quenching or chemical reaction is now also being investigated by monitoring the Cl-atom concentration in its $^2P_{3/2}$ and $^2P_{1/2}$ states by resonance absorption at 134.7 and 136.3 nm.[8] Early results indicate extensive reaction, i.e., a sharp rise of the Cl-absorption signal leveling off at a constant value as more Cl_2 is added. The Cl-atom yield, the $^2P_{1/2}$ to $^2P_{3/2}$ concentration ratio, and the contribution of the $NCl + N(^4S) \rightarrow N_2 + Cl$ reaction are still under investigation.

Potentially interfering reactions of $N(^2D, ^2P)$ are easily shown to be much too slow to perturb the observed N-metastable decays. The present experiments thus provide species-selective, elementary reaction rate constants at 298 K, and they are easily extendable to higher and lower temperatures. They show the considerable power of the flow tube technique in the study of bimolecular reactions.

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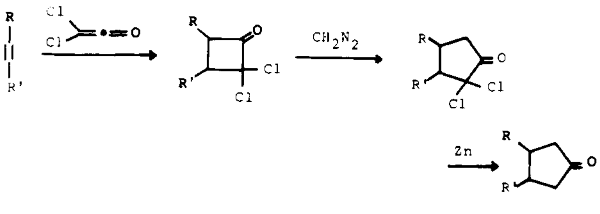
A Versatile Three-Carbon Annelation. Synthesis of Cyclopentanones and Cyclopentanone Derivatives from Olefins[1]

Sir:

Four-carbon annelation reactions have been extensively studied and are of general importance in the construction of complex organic molecules.[2] In contrast, there are few *generally useful* three-carbon annelation processes,[2,3] in spite of the widespread presence of the cyclopentane ring in many classes of natural products. In this communication, we present a simple, yet versatile, synthesis from olefins of cyclopentanones and various cyclopentanone derivatives, which we believe will offer an attractive alternative to existing three-carbon annelation methods.

The procedure (eq 1), formally a [3 + 2] cycloaddition, is



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