PHOTOCHEMISTRY OF SMALL MOLECULES

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1. Introduction

There is of course no sharp distinction between small molecules and others. Atoms exhibit a unique feature in that only pure electronic states are possible. Diatomic molecules are restricted to a single vibrational and a doubly degenerate rotational degree of freedom, and if a bond is broken on light absorption two atoms are formed. Simple discriminations do not extend to higher polyatomic molecules except in special cases. Although the domain of small molecules is arbitrary, photochemists seem to know when they are in it. Perhaps they believe it is a domain in which the possible photophysical and photochemical primary and secondary processes are few enough to allow for the hope of approaching a complete description.

In the first volume of the *Journal of Photochemistry*, 50 manuscripts were published of which 24 reported studies on small molecules, five or fewer atoms. I find it interesting to survey three systems pertinent to the light-absorbing species in three of these papers: an atom, Hg [1]; a diatomic molecule, NO [2]; a polyatomic molecule, H_2O_2 [3].

2. Mercury ($6\,^3P_1$) reaction with hydrogen

The absorption by mercury of mercury resonance radiation $6\,^3P_1 \rightarrow 6\,^1S_0$ (253.7 nm) in the presence of molecular hydrogen to yield hydrogen atoms has been known for over 60 years. The mechanism and quenching cross section are of considerable interest for understanding pure electronic energy transfer and reaction channels. Although hydrogen atoms are formed two mechanisms seemed to be possible:

$$Hg(^3P_1) + H_2 \longrightarrow Hg(^1S_0) + 2H \tag{1}$$

$$Hg(^3P_1) + H_2 \longrightarrow HgH + H \tag{2}$$

The presence of HgH was shown by light absorption in the flash-photosensitized reaction [4]. Later work showed that both reactions occur, that the quantum yield for reaction is 0.93, and hence that non-reactive deactivation to the $^1S_0$ state was of minor importance, and that the fraction of reaction

yielding the hydride was 0.67 for hydrogen and 0.76 for deuterium [5]. These results differ widely from predictions made from phase space theory of quantum yields of 0.16 for HgH, 0.52 for the hydrogen atom and 0.58 for vibrationally hot molecular hydrogen [6].

The reaction is often used to synthesize hydrogen atoms. Therefore, it is of interest to know the rate constant for

$$HgH + M \longrightarrow Hg + H \tag{3}$$

In gaseous mixtures of hydrogen, NO and mercury irradiated at 253.7 nm both hydrogen atoms and HgH are precursors of $HNO(^1A'')$ chemiluminescence. With isobutene added hydrogen atoms are scavenged and the phase shift between modulated 253.7 nm light and the chemiluminescence yields the rate of HgH decomposition [7]. At 298 K and with M being mainly molecular hydrogen, $k_3 = 4.8 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}. For the reaction

$$HgH + NO \longrightarrow HNO(^1A'') \tag{4}$$

this work yields $k_4 = 4.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Cross sections, or rate constants from which they are calculated, for $Hg(^3P_1)–H_2$ collisions have been measured for over 50 years, usually by monitoring fluorescence from the $^3P_1$ state. However, using measurements of Lyman α absorption of the product hydrogen atoms, Hong and Mains [1] found cross sections of 1.0 and 1.1 nm^2 for molecular hydrogen and for HD, or the same within experimental error. Using a light pulser with a 40 ns pulse width at 253.7 nm, Hikida et $al.$ [8] reported $k_{q1} = 4.7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, equivalent to a quenching cross section of 0.84 nm^2.

Quenching of the metastable $Hg(6\,^3P_0)$ state by molecular hydrogen studied by monitoring 253.7 nm emission following flash excitation by 253.7 nm light with nitrogen in the system to promote $^3P_0$ formation yields $k_{q0} = 5.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K [9]. Studies in the system $Hg–H_2–N_2$ subjected to repetitive 253.7 nm pulse followed by laser excitation at 404.7 nm, $Hg(7\,^3S_1) \leftarrow Hg(6\,^3P_0)$, and monitored by measuring 546.1 nm, $Hg(7\,^3S_1) \rightarrow Hg(6\,^3P_2)$, fluorescence gave $k_{q0} = 5.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [10]. The calculated average cross section from these two studies is 0.0093 nm^2.

3. NO photolysis

The detailed mechanism for the photodissociation of NO is strongly wavelength dependent. From the ground state, $X\,^2\Sigma$, light absorption correlates with the following states: $A\,^2\Sigma^+$, 196 - 227 nm; $B\,^2\Pi$, 160 - 206 nm; $C\,^2\Pi$, $D\,^2\Sigma^+$, $E\,^2\Sigma^+$, 138 - 192 nm. The threshold for bond rupture is 191 nm. Ground state $N(^4S)$ and $O(^3P)$ atoms are formed by predissociation from the $A\,^2\Sigma^+$, $B\,^2\Pi$ and $C\,^2\Pi$ states through the repulsive $^2\Sigma^+$ state or the bound $a\,^4\Pi$ state [11].

From studies below the dissociation threshold it was concluded that the $A\,^2\Sigma^+$, $v = 1$, but not the $v = 0$ state gave chemical reaction [12]. Later work

at 213.9 nm, $v = 1$, and 226.5 nm, $v = 0$, shows that this is incorrect and that both states exhibit the same reactivity [2]. The following reaction scheme is proposed:

$$NO^* + NO \longrightarrow N_2O_2 \tag{5}$$

$$N_2O_2 \longrightarrow N_2 + O_2 \tag{6}$$

$$N_2O_2 \longrightarrow N_2O + O \tag{7}$$

$$N_2O_2 \longrightarrow 2NO \tag{8}$$

$$N_2O_2 + NO \longrightarrow N_2 + O_2 + NO \tag{9}$$

$$N_2O_2 + NO \longrightarrow N_2O + NO_2 \tag{10}$$

NO^* represents either the $A\,^2\Sigma^+$ state, the $a\,^4\Pi$ state or the ground state in high vibrational levels. N_2O_2 is an energy-rich dimer of NO [13], and may not exist except in the sense of an NO^*–NO collision, but invoking it leads to easier correspondence to the rate law.

In the far UV where bond breaking occurs either directly or by predissociation the following scheme explains the results:

$$N + NO \longrightarrow N_2 + O \tag{11}$$

$$O + NO + M \longrightarrow NO_2 + M \tag{12}$$

$$O + O + M \longrightarrow O_2 + M \tag{13}$$

N_2O is also a product, probably formed by the reaction of nitrogen atoms with NO_2 [14, 15]. An average from studies by discharge flow resonance fluorescence and by flash photolysis resonance fluorescence (FPRF) techniques gives $k_{11} = 3.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} between 196 and 400 K [16]. Pulsed laser photolysis of NO followed by monitoring NO_2 chemiluminescence gives $k_{12} = 1.2 \times 10^{-31}$ cm^6 molecule^{-2} s^{-1} for NO as M at 298 K [17].

4. H_2O_2 photolysis

The mechanism for the photolysis of H_2O_2 at 253.7 nm and 298 K is simple [18]:

$$H_2O_2 + h\nu \longrightarrow 2OH \tag{14}$$

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \tag{15}$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \tag{16}$$

The experimental dissociation quantum yield is 1.7, within experimental error of the mechanism maximum of 2. The threshold for the production of $OH(A^3\Sigma)$ is 200 nm but pulsed laser experiments at 193 and 243 nm show only the formation of $v = 0$ ground state $OH(X^2\Pi)$ with equal populations of $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ [19]. At 243 nm about 268 and 13 kJ mol^{-1} and at 193 nm about 1150 and 33 kJ mol^{-1} are released as translational and rotational energy on the average.

The first determination of k_{15}, using the flash photolysis kinetic spectroscopy technique, gave 9.3×10^{-13} cm^3 $molecule^{-1}$ s^{-1} [20]. A study of the photochemistry of H_2O_2 with added CO gave $k_{15} = 1.2 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} from competitive kinetics [3]. Subsequent studies yielded lower values in the range $(6 - 8) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} but the average of six recent studies [21, 22], mostly using the FPRF method, gives $(1.68 \pm 0.24) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Hydrogen atoms are formed in photolysis at 123.6 nm [23] and also in the photolysis at 253.7 nm with CO present [3]:

$$OH + CO \longrightarrow CO_2 + H \tag{17}$$
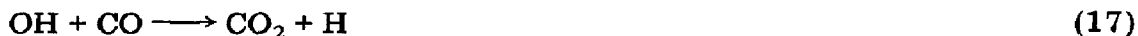
Two reactions with H_2O_2 are probable:

$$H + H_2O_2 \longrightarrow H_2O + OH \tag{18a}$$

$$H + H_2O_2 \longrightarrow H_2 + HO_2 \tag{18b}$$

Competitive kinetics with CO present yield $k_{18a} = 5.7 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} and $k_{18b} = 3.1 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} [24]. The only other experimental determination, the FPRF method, gives $k_{18} = 5.3 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} [25], six times higher. More recent qualitative results [26] are in accord with the lower value.

5. Conclusions

Although only three examples are discussed in this survey the implications are general. For mercury excited at 253.7 nm in reaction with molecular hydrogen two reaction channels are identified, but a prediction from theory is not in accord. Now that the experimental results are known, theory has a goal which it probably will achieve in the near future. The photolysis of NO presents the problem of differentiating between atomic and excited molecule reactions. As much of the photophysics and many of the rate constants are known, further progress should come from computer modeling in delineated systems of interest. The photolysis of H_2O_2 from 190 to 254 nm yields only vibrationless ground state OH but at 124 nm hydrogen atoms are formed. The rate constant for OH with H_2O_2 is well established but two studies of hydrogen atoms with H_2O_2 disagree. This disagreement should certainly give impetus to further experiments because of the importance of the reaction in atmospheric chemistry.

Perceived societal needs are a strong factor in determining the direction of research. Hence we can expect that in the photochemistry of small molecules major emphasis will be directed at molecules of interest in atmospheric chemistry. The number of these molecules is large: an incomplete list of those limited to stratospheric interest [27] gives 157 reactions of which only six involve molecules having more than five atoms and 48 of which are photochemical.

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