products are often written as the corresponding peroxy radicals. Also, acylate radicals will decompose rapidly to give an alkyl radical and CO_2 . Therefore, only alkoxyl, peroxyalkyl, and peroxyacyl radicals need to be considered explicitly in terms of NO_x chemistry. Table 6-1 shows the various raction combinations that are important between these radicals and NO and NO₂.

The reactions of HO with NO_2 and NO are reasonable well understood and have been previously listed as reactions 6-18 and 6-19. Rate constants for these two reactions are available.⁹

The rate constant for the reaction of HO_2 and NO has recently been determined by direct means and is substantially larger than previously calculated indirectly.¹⁹ The HO_2 -NO reaction, as noted earlier, is a key reaction in the atmospheric conversion of NO to NO₂.

The reaction of HO_2 and NO_2 has the following two possible mechanisms.²⁰ Reaction 6-35b is not considered to be important in atmospheric chemistry:

$$HO_2 + NO_2 \rightarrow HO_2 NO_2$$
 (6-35a)

 $HO_2 + NO_2 \rightarrow HONO + O_2$ (6-35b)

In addition, the peroxynitric acid formed in reaction 6-35a thermally decomposes as follows:²¹

and

 $HO_2NO_2 \rightarrow HO_2 + NO_2$ (6-36)

At the present time it appears that, at the temperatures prevalent in summer smog episodes (>20°C), peroxynitric acid