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FLASH PHOTOLYSIS-SHOCK TUBE STUDIES

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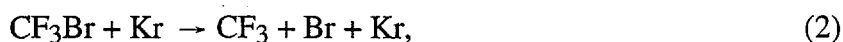
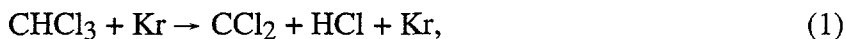
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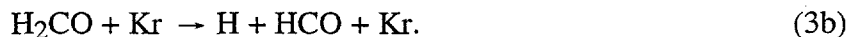
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Following earlier investigations on the dissociation rates of halogen containing molecules,¹⁻¹⁴ we studied the thermal decompositions of CHCl_3 ¹⁵ and CF_3Br .¹⁶ In addition, we measured the branching ratio and rate constants for the thermal decomposition of H_2CO .¹⁷ We studied three bimolecular rate processes: $\text{H} + \text{H}_2\text{CCO}$,¹⁸ $\text{CF}_3 + \text{H}_2$, and $\text{H} + \text{CF}_3\text{H}$.¹⁹

Decomposition studies in reflected shock waves on three reactions were completed using atomic resonance absorption spectroscopic (ARAS) detection and/or (with J. H. Kiefer and associates) the laser schlieren density gradient (LS) method. These are:



and



Rate constants for the thermal decomposition of CHCl_3 were measured by the LS method over the T-range, 1282-1878 K, giving the second-order result,¹⁵

$$k_{\text{CHCl}_3} = 7.073 \times 10^{-8} \exp(-22516 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. (\pm 15\%) \quad (4)$$

Two unimolecular theoretical approaches were used to rationalize this result. Best fits were obtained with threshold energy and energy transfer parameters, $E_0 = 56.0 \text{ kcal mole}^{-1}$ and $\langle \Delta E \rangle_{\text{down}} = (820 \pm 30) \text{ cm}^{-1}$, respectively. $[\text{Cl}]_t$ was additionally measured using Cl-atom ARAS, and the results were rationalized by considering the various reactions of CCl_2 .

We determined an experimental curve-of-growth for Br-atoms and subsequently used it for quantitative determinations of $[\text{Br}]_t$ in the evaluation of thermal dissociation rate constants for reaction (2).¹⁶ These rate constants were measured over the temperature range, 1222-1624 K. The results can be expressed in second-order by

$$k_{\text{CF}_3\text{Br}} = 8.147 \times 10^{-9} \exp(-24488 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. (\pm 33\%) \quad (5)$$

Under the present conditions, unimolecular theory was used to rationalize the data showing that the reaction was between 30-53% of the low pressure second-order limit. The results were fitted with the known threshold energy, $E_0 = 70.1 \text{ kcal mole}^{-1}$, by varying $\langle \Delta E \rangle_{\text{down}}$. The best fit required $\langle \Delta E \rangle_{\text{down}} = 550 \text{ cm}^{-1}$.

Experiments, between 2005-2367 K, on reaction (3) utilized quantitative H-atom ARAS.¹⁷ $[H]_t$ was observed using two different sources of H_2CO (purified from paraformaldehyde and from purified trioxane). The profiles were fitted by chemical simulations yielding the second-order results:

$$k_{H_2CO}^{3a} = 4.658 \times 10^{-9} \exp(-32110 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, (\pm 29\%) \quad (6)$$

and,

$$k_{H_2CO}^{3b} = 1.019 \times 10^{-9} \exp(-38706 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. (\pm 21\%) \quad (7)$$

Three theoretical unimolecular rate approaches were used to rationalize the data; however, in this case, the data were fitted by only varying $-\langle\Delta E\rangle_{all}$'s since threshold energies for both processes are known with high accuracy. Using single channel analysis for the reactions, the calculations show that both are at the low pressure limit under the present conditions. For $E_0^{3a} = 79.2$ and $E_0^{3b} = 86.705 \text{ kcal mole}^{-1}$, $-\langle\Delta E\rangle_{all}^{3a} = 390$ and $-\langle\Delta E\rangle_{all}^{3b} = 119 \text{ cm}^{-1}$, respectively, are required to fit the data. In an attempt to understand the effects of depopulation on (3b) due to the presence of (3a), we attempted a multichannel analysis using the *Unimol* code. If the absolute values for (3a) are fitted (using $-\langle\Delta E\rangle_{all}^{3a} = 333 \text{ cm}^{-1}$), then the predicted rate constants for (3b) are only about 7% of those measured, suggesting that the theory seriously overestimates the effects of depopulation.

We measured the bimolecular rate constants for,



over the T-range, 863-1400 K.¹⁸ This is a chemical activation reaction with a positive barrier and a dissociation channel that is lower lying than reactants. Hence, the results can be identified with the high pressure limit. We obtained the Arrhenius result,

$$k_{H+H_2CO} = (4.85 \pm 0.70) \times 10^{-11} \exp(-2328 \pm 155 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (9)$$

The present results were combined with earlier data, and the combined database was theoretically interpreted using conventional transition state theory with Eckart tunneling. A modified *ab initio* transition state structure was indicated before the data could be reproduced.

With the H-atom ARAS technique, we measured the rate constants for the reactions,¹⁹



and,



The respective results expressed in Arrhenius form are:

$$k_{CF_3+H_2} = 2.56 \times 10^{-11} \exp(-8549 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (12)$$

and,

$$k_{H+CF_3H} = 6.12 \times 10^{-11} \exp(-7363 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (13)$$

Over the common range of temperature overlap, these can be combined to yield the equilibrium constant for the reaction. We find that the Janaf values for molecular parameters and enthalpy change, $\Delta H_0^0 = -1.564 \text{ kcal mole}^{-1}$, give equilibrium constants that are in excellent agreement with those implied by Eqs. (12) and (13). Hence, the data for reaction (11) have been transformed through the equilibrium constants to extend the database for reaction (10). These are then combined with lower temperature values to give a rate constant database from near room temperature to 1600 K. An *ab initio* structure for the transition state then has allowed for a rationalization of this extended database.

Data have also been obtained for the photodissociation quantum yield at 193 nm in ketene (with G. P. Glass) and the reaction: $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{O}$. CH_3 profiles have also been measured at 214 nm using the recently described multipass optical system.²⁰ Though complete, these data are still being analyzed.

Additional atom and radical with molecule reaction studies (e. g. $\text{Cl} + \text{hydrocarbons}$, $\text{OH} + \text{hydrocarbons}$, $\text{I} + \text{H}_2$, $\text{CF}_2 + \text{O}_2$, etc.) and, also, thermal decomposition investigations (e. g. C_2H_5 , C_2H_3 , etc.) are either partially completed or in the planning stage at the present time. These reaction studies are of theoretical interest to chemical kinetics and of practical interest in hydrocarbon combustion or waste incineration.

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