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FLASH PHOTOLYSIS-SHOCK TUBE STUDIES

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Following earlier investigations on the dissociation rates of CF_3Cl,[1] CF_2Cl_2,[2] $CFCl_3$,[3] and CCl_4,[4] we systematically applied theory to explain the rate behavior for the this homologous series.[5] Three different unimolecular theoretical methods were compared. The inferred results were in good agreement with one another suggesting that the conclusions are not strongly dependent on the degree of theoretical rigor. In all of these cases and in others,[6-12] we have determined the best mutual values for both threshold energy, E_0, and energy transfer parameter, $\langle \Delta E \rangle_{down}$. The best fits generally give values for E_0 that are in good agreement with other thermochemical methods. Also, for halogen containing molecules, the derived $\langle \Delta E \rangle_{down}$ values are large, giving effective collisional efficiency factors, β_c, between ~0.02 and 0.10 at 1300 K.

During the past year, thermal decomposition studies in reflected shock waves on two reactions were completed using the I-atom atomic resonance absorption spectroscopic (ARAS) detection method; i. e.,

$$CH_3I + Kr \rightarrow CH_3 + I + Kr, \qquad (1)$$

and,

$$C_6H_5I + Kr \rightarrow C_6H_5 + I + Kr. \qquad (2)$$

Rate constants for reaction (1) were measured over the temperature range, 1052-1616 K.[13] With the experimental curve-of-growth for the I-atom ARAS technique that had been previously determined,[11] the yield of atoms (i. e., the number of I-atoms formed per dissociating molecule) was found to be unity. The results can be expressed in second-order by

$$k_{CH_3I} = 4.36 \times 10^{-9} \exp(-19858\ K/T)\ cm^3\ molecule^{-1}\ s^{-1}\ (\pm 36\%) \qquad (3)$$

Two unimolecular theoretical approaches were use to rationalize the data. These showed that the reaction was effectively in the low pressure second-order limit under the present conditions. The results were fitted with the known threshold energy, E_0 = 55.5 kcal mole^{-1}, by varying $\langle \Delta E \rangle_{down}$. The best fit required $\langle \Delta E \rangle_{down}$ = 590 cm^{-1}.

Experiments on reaciton (2) also gave I-atom yields of unity showing that this decomposition is an excellent source for preparing phenyl radicals for subsequent reaction studies of this species.[14] The results can be expressed in first-order by

$$k_{C_6H_5I} = 1.982 \times 10^{11} \exp(-23120\ \mathrm{K/T})\ \mathrm{s}^{-1}\ (\pm 60\%) \qquad (4)$$

over the temperature range, 1082 to 1466 K. Again, two unimolecular rate theoretical approaches were used to rationalize the data; however, in this case, the data were fitted by mutually varying both E_0 and $\langle \Delta E \rangle_{down}$. The calculations show that the reaction is much closer to the high pressure than to the low pressure limit under the present conditions. Averaging both methods, we conclude that $E_0 = (66.7 \pm 0.7)$ kcal mole^{-1} and $\langle \Delta E \rangle_{down} = (447 \pm 92)$ cm^{-1}. This suggests $\Delta_f H^0_{C_6H_5,0K} = 83.4$ kcal mole^{-1}, in agreement with other accepted values, within experimental error.

Phenyl-radical dissociation experiments were then studied using the H- and I-atom ARAS techniques.[15] With ppm quantities of iodobenzene in Kr, both atomic species were monitored between 1358 and 1548 K. The results showed that I-atoms almost instantaneously form and do not react further on the time scale of the experiment. The H-atom ARAS experiments showed that phenyl-radicals dissociate to H + C_6H_4 (or C_2H_2 + C_4H_2). H-atom profiles were measured over the pressure range, 398 to 488 Torr, and these showed that H-atoms subsequently react with phenyl to produce benzene. The profiles could be fitted to the two step mechanism giving estimates for the rate constants: C_6H_5 (+Kr) → H + C_6H_4 (+Kr); k = 1.36 x 10^{15} exp(-42156 K/T) s^{-1} and H + C_6H_5 (+Kr) → C_6H_6 (+Kr); k = (3.3 ± 1.2) x 10^{-10} cm^3 molecule^{-1} s^{-1}, respectively.

Experiments were then performed at lower temperatures (1068 to 1403 K) with O_2 added to the iodobenzene-Kr mixtures.[15] ARAS observations unambiguously showed that I-atoms do not react on the time scale of the experiments with O_2 or with any other radicals produced in the system. The H-atom ARAS experiments indicated an enhanced formation rate over that due solely to phenyl dissociation. Absolute [H] measurements showed that ~33% of the initial phenyl yielded H-atoms in the phenyl + O_2 reaction. Absolute O-atom ARAS measurements showed that ~67% of the phenyl-radicals were depleted to produce phenoxy, C_6H_5O, and O-atoms. Following direct formation from phenyl + O_2, both $[H]_t$ and $[O]_t$ showed slight maxima indicating some secondary atom-radical recombination reactions. These features were included in a ten step mechanism that concurs with that of Frank et al.[16] The final fits yielded values for the rate constants: C_6H_5 + O_2 → H + $C_6H_4O_2$; k = 4.98 x 10^{-11} exp(-4520 K/T) and C_6H_5 + O_2 → O + C_6H_5O; k = 4.32 x 10^{-11} exp(-3080 K/T), both in cm^3 molecule^{-1} s^{-1}. These data are theoretically rationalized along with earlier data and theory.[17,18]

Data have also been obtained for the photodissociation quantum yield at 193 nm in ketene (with G. Glass), the branching ratio for the thermal dissociation of CH_2O, the reaction: H + CH_2CO, and the reaction: CH_3 + O_2 → CH_3O + O. CH_3 profiles have also been measured at 214 nm using the recently described multipass optical system.[19] Though complete, these data are still being analyzed. Lastly, experimental results and calculations on the thermal decomposition of $CHCl_3$ and the subsequent reactions of CCl_2 radicals are nearly complete.

Additional atom and radical with molecule reaction studies (e. g. Cl + hydrocarbons, OH + hydrocarbons, I + H_2, CF_3 + H_2, CF_2 + 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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