Communication: Kinetics of the Reaction of C₆H₅ with HBr

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Abstract

The rate constant for the reaction of phenyl radical with hydrogen bromide has been measured with the cavity-ring-down method at six temperatures between 297 and 523 K. The Arrhenius expression for the H abstraction reaction can be effectively given by:

$$k_{\phi} = 10^{-10.39 \pm 0.10} \exp[-(551 \pm 19)/T] \,\mathrm{cm}^3/\mathrm{s}$$

The values of these parameters are similar to those for the H + HBr reaction, but are in sharp contrast to those for alkyl radical reactions. The gross difference between the alkyl radical reactions and the phenyl and H-atom reactions could be rationalized in terms of the inductive effects of these radicals as measured by Taft's σ^* (polar) constants. © 1993 John Wiley & Sons, Inc.

In a recent series of studies, Gutman and co-workers [1-3] have shown that the reaction of alkyl radicals with HBr occurs with a strong negative temperature dependence. The measured activation energies vary from -0.5 kcal/mol for CH₃ to as large as -1.9 kcal/mol for t-C₄H₉ according to more recent reports [3,4].

The reaction of H atoms with HBr, on the other hand, has been shown to take place with a small positive activation energy, 0.62-0.91 kcal/mol, according to the results of several investigations [5-7]. The absolute value of the rate constant for the reaction is, however, comparable to those for the alkyl reactions [3,4].

The surprisingly large "negative activation energies" observed for these alkyl reactions could be qualitatively attributed to the well-known electrondonating (+I) effect of the alkyl groups [8], which gives rise to a strong polar interaction, $R \cdots H^+ - Br^-$, during the course of the reactions. In fact, a complex-forming mechanism assuming the presence of a short-lived RHBr intermediate has been invoked to account for the observed negative temperature dependency [1-4,9,10]. The H atom, which does not have a strong electron-donating effect, is therefore expected to behave normally with a small positive activation energy [5-7].

In this study, we have investigated the reaction of the C_6H_5 radical with HBr using a new resonance absorption technique [11–13]. The applicability of this technique has been tested with the well-known NH_2 + NO reaction [14], with excellent agreement between the measured bimolecular rate

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International Journal of Chemical Kinetics, Vol. 25, 875–880 (1993) © 1993 John Wiley & Sons, Inc. CCC 0538-8066/93/100875-06 constant $(1.4 \pm 0.2 \times 10^{-11} \text{ cm}^3/\text{s})$ and the recommended literature value $(1.6 \times 10^{-11} \text{ cm}^3/\text{s})$ at 297 K. The great sensitivity and selectivity of this technique allows us to measure absolute rate constants for many C₆H₅ radical reactions at room temperature down to ca. $10^{-17} \text{ cm}^3/\text{s}$ [13]. The effect of temperature on the rate of the C₆H₅ + HBr reaction, measured for the first time in this work, will be discussed with reference to the aforementioned R + HBr reactions. These results will be correlated with the known inductive effects of the R-groups in terms of Taft's σ^* polar constants [15].

Because the experimental setup for the present kinetic measurement has just been published in the literature [13], it is briefly described as follows: Two pulsed lasers were employed for kinetic measurement. The first, photolytic laser (KrF, 248 nm) was introduced into the reaction system through two quartz windows crossing each other at the center of a heated flow-tube reactor. The second, probing laser (Laser Photonics N2-laser pumped dye laser, FWHM = 8 ns), was injected into the system between the two dissociation beams and overlapping with them at the center of the reactor, at different time-intervals after photo-dissociation, to probe the C_6H_5 radical through one of the two highly reflective mirrors (R = 0.9999with 6 m radius of curvature) enclosing the reactor. The mirrors were optically aligned with a He-Ne laser to form a low-loss resonating cavity. The concentration of the C_6H_5 radical produced from the photolysis of C_6H_5NO was measured in terms of the decay time of the injected dye laser pulse, detected with a photomultiplier tube located behind the second mirror.

The decay time of the probing laser pulse was significantly lengthened over its original pulse width (from 8 ns to about 30 μ s) due to oscillation inside the cavity. The presence of an absorbing species (such as C₆H₅ at 504.8 nm) shortens the decay time which can be described by the following eq. [16]:

(1)
$$-d\Phi/dt = \Phi(\alpha cl/nL + 1/t_c^0)$$

where Φ is the number of photons injected into the optical cavity, t_c^0 is the photon decay time in the absence of an absorbent whose absorption coefficient is α at the probing wavelength, c is the velocity of light, n is the index of refraction of the absorbing medium with width l, and L is the cavity length formed by the two mirrors. Integration of eq. (1) at constant α gives

(2)
$$\Phi = \Phi_0 \exp(-t/t_c)$$

where

$$1/t_c = \alpha c l/nL + 1/t_c^0$$

or

$$(3) 1/t_c - 1/t_c^0 = \alpha c l/nL$$

The absorption coefficient α in eq. (3) is the product of the radical extinction coefficient, ε , and its concentration, $[R]_{t'}$, at t' after photoinitiation. Since the photon decay time ($t_c \leq 30 \ \mu s$) is much shorter than the radical decay time (typically $1 \leq t' \leq 50$ ms), the integration of eq. (1) performed above

was made by assuming a constant value of α within the photon decay time. Substituting the relationship, $\alpha = \varepsilon[R]_{t'} = \varepsilon[R]_0 \exp(-k^{\mathrm{I}}t')$, into eq. (3), we obtain

$$1/t_c - 1/t_c^0 = (cl\varepsilon/nL)[R]_0 \exp(-k^{\mathrm{I}}t')$$

or

(4)
$$\ln(1/t_c - 1/t_c^0) = B - k^1 t'$$

where $B = \ln(cl\varepsilon/nL)$ and k^{I} is the first-order decay constant of the radical (with an initial concentration $[R]_{0}$) measured in the presence of an excess amount of a molecular reactant such as HBr.

The linear relationship between $\ln(1/t_c - 1/t_c^0)$ and the reaction time, t', for the reaction of C_6H_5 with HBr is illustrated in Figure 1. The photon decay times, t_c and t_c^0 , were measured with the photolysis laser turning on and off, respectively. The slopes of the $\ln(1/t_c - 1/t_c^0)$ vs. t' plots give the pseudo-first-order decay constants for C_6H_5 in the presence of different (excess) amounts of HBr. The absolute values of the second-order rate constant, k^{II} , for the C_6H_5 + HBr reaction were obtained, in turn, from the slopes of the k^{I} vs. [HBr] plots as presented in Figure 2 for three different reaction temperatures. A least-squares analysis of all measured k^{II} 's at six temperatures between 297 and 523 K gave the following Arrhenius equation:

$$k_{\phi} = 10^{-10.39 \pm 0.10} \exp[(-551 \pm 19)/T] \text{ cm}^3/\text{s}.$$

The deviations quoted in the equation represent 2σ 's.

It is interesting to note that the Arrhenius parameters of our rate constant for $C_6H_5 + HBr$, contrary to those for the alkyl radical reactions [3,4], are very similar to those of H + HBr reported by several groups [5–7]. The clear difference between these two groups of radicals, alkyls vs. H and phenyl, as alluded to in the introductory section, could be attributed to the electron-donating power (the +I-effect) of these radicals. Because the whole series of the metathetical reactions, $R + HBr \rightarrow RH + Br$ (R = H, CH_3 , C_2H_5 , *i*- C_3H_7 , *t*- C_4H_9 , and C_6H_5), which have been quantitatively studied to date, involve the transfer of H and the H atom in HBr is positively charged, the interaction of HBr with the alkyl groups is expected to be much stronger, particularly with *t*- C_4H_9 , than with H or C_6H_5 . The latter is known to exhibit the negative I-effect in a number of organic reactions [8].

One of the best quantities to characterize the inductive effect of various aliphatic substituents is Taft's σ^* (polar) values derived from the rate constants for the acid or base-catalyzed hydrolysis of substituted esters [15]; for example,

$$\begin{array}{c} O & O^{-} & O \\ \parallel & & \\ R - COR' + OH^{-} \longrightarrow R - C - OR' \longrightarrow RCOH + R'O^{-} \\ & & \\ OH \end{array}$$



Figure 1. Typical pseudo-first-order decay plots for the C_6H_5 reaction under different, excess HBr concentration conditions. (\bigcirc)—[HBr] = 0, (\triangle)—[HBr] = 8.65 × 10¹³, (\bigcirc)—[HBr] = 2.70 × 10¹⁴, (\diamondsuit)—[HBr] = 2.82 × 10¹⁴ all in molecules/cm³. The slopes of these plots give the first-order decay constants, k^1 .



Figure 2. The $k^{\rm I}$ vs. [HBr] plots at different temperatures. (\Box) T = 297 K, $k = (5.82 \pm 0.37) \times 10^{-12} \, {\rm cm}^3/{\rm s}, (\bigcirc) T = 373$ K, $k = (9.95 \pm 0.55) \times 10^{-12} \, {\rm cm}^3/{\rm s},$ and (\triangle) T = 473 K, $k = (12.8 \pm 0.8) \times 10^{-12} \, {\rm cm}^3/{\rm s}$. The slopes of these straight lines give the second-order rate constants for the C₆H₅ + HBr reaction, $k^{\rm II}$.

In these reactions, the electron-donating or withdrawing effects of substituent (R) groups have a strong influence on the rates of the hydrolysis reactions.

In Figure 3, we have plotted the experimentally measured activation energies for the R + HBr reactions against Taft's σ^* values given by Laidler [15] for the various R-groups. The activation energies for these simple abstraction reactions strongly correlate with the electron-donating or withdrawing properties of the attacking radicals. Those with positive σ^* values, such as H and C₆H₅, react with HBr with positive activation energies, whereas the ones with zero or negative σ^* values have negative activation energies.

Recently, Wine and co-workers, in two separate studies [17,18], have measured the rate constants for the reactions of HBr with $O({}^{3}P)$, $Cl({}^{2}P)$, HS, and CH₃S. The activation energies for these reactions are, respectively, 2.9, 0.8, 1.9, and 0.8 kcal/mol. Although the σ^{*} values of the O, Cl, HS, and CH₃S substituents associated with the type of hydrolysis reactions mentioned above are not known, they must be positive, on grounds that the related inductive substituent constants of the latter three groups (Cl, HS, and CH₃S) are all positive, whereas those of the alkyl groups are all negative. This suggests that the correlation shown in Figure 3 for the hydrocarbon radicals is also qualitatively applicable to these four reactions.

Experiments are underway to investigate the kinetics of the C_6H_5 radical reactions with a variety of molecules, including DBr, HCl, DCl, and, most importantly, combustion-related species, in order to understand the chemical reactivities of this important prototype aromatic radical.



Figure 3. The correlation of the measured activation energies for the $R + \text{HBr} \rightarrow R\text{H} + \text{Br}$ reactions with Taft's σ^* (polar) values as summarized in ref. [15]. (\bigcirc)—This work, (+)—ref. [5], (\bigcirc)—ref. [6], (\bigcirc)—ref. [7], (\square)—ref. [3], and (\triangle)—ref. [4].

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