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Kinetics for the Recombination of Phenyl Radicals

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The rate constant for the $C_6H_5 + C_6H_5$ recombination reaction has been determined in the temperature range 300−500 K using a laser photolysis/mass spectrometric technique. The result is represented by $k_1 = (1.39 \pm 0.11) \times 10^{13} e^{-(56\pm36)/T}$ cm^3/(mol s). In addition, the rate constant for the $C_6H_5 + C_6H_5NO$ association reaction was found to be $k_4 = (4.90 \pm 0.19) \times 10^{12} e^{(34\pm16)/T}$ cm^3/(mol s) by the mass balance of the initial concentration of C_6H_5 radicals. Using the result of k_1, previous kinetic data for C_6H_5 reactions determined by the conventional relative rate method were reanalyzed.

Introduction

Phenyl radical is one of the most important reactive species in the combustion of hydrocarbons, particularly in relation to the formation of polycyclic aromatic hydrocarbons (PAH's) and the combustion of lead-free gasoline in which small aromatics are used as additives.[1−5] Prior to our recent use of the cavity-ring-down (CRD) method[6−15] for direct determination of rate constants of various C_6H_5 reactions in the gas phase, most kinetic data were analyzed by using the recombination of phenyl radicals as a reference process:[16−19]

$$C_6H_5 + C_6H_5 \xrightarrow{k_1} C_{12}H_{10} \text{ (biphenyl)} \qquad (1)$$

Experimentally, the products of C_6H_5 metathetical reactions, for example C_6H_6 from its reaction with H_2,

$$C_6H_5 + H_2 \xrightarrow{k_2} C_6H_6 + H \qquad (2)$$

were determined together with biphenyl; the rate constant for the abstract process was then calculated with the much-used relationship[16−19]

$$k_2 = (k_1/[C_{12}H_{10}])^{1/2}[C_6H_6]/[H_2]$$

using an assumed "reasonable" value for k_1. However, the value of k_1 has been chronologically reduced from 1×10^{14} (ref 17) to 1×10^{13} (ref 19) to 3×10^{12} cm^3/(mol s) in most recent analyses of high-temperature kinetic data by Stein and co-workers.[18] This historic change reduces the values of k_2's by as much as 580%.

In view of the uncertainty in k_1 and its pronounced effect on the magnitude of many rate constants measured to date for C_6H_5 reactions (some of which are too slow to be determined directly by the CRD technique, e.g., $C_6H_5 + CH_4$), we have carried out a series of kinetic measurements for k_1 using a laser photolysis−mass spectrometric technique.[20,21] The results of this study for k_1 and the reanalyzed kinetic data for many of the C_6H_5 reactions determined by the conventional relative rate method are reported herein.

Experimental Section

The rate constant for the recombination of C_6H_5 radicals has been measured at five temperatures between 300 and 500 K using the laser photolysis/high-pressure mass spectrometric sampling system recently employed for product branching studies of NH_2 reactions with NO[20] and NO_2.[21] The configuration of the quartz reaction tube, which has a 120 μm conical supersonic sampling hole at the center of the tube, is similar to that described by Saalfeld and co-workers,[22,23] and the coupling of the photodissociation excimer laser with the reactor is essentially the same as that used by Gutman and collaborators.[24,25] A schematic diagram of the apparatus and the procedure of product measurements have been presented in greater detail in the preceding article.[26]

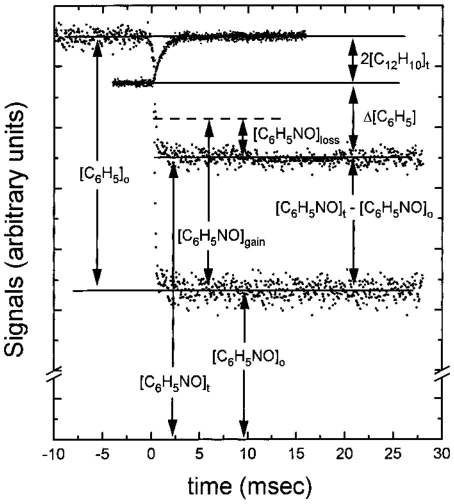

Figure 1. Typical time-resolved mass spectrometric transient signals of $C_{12}H_{10}$ and C_6H_5NO. See text for explanation.

The C_6H_5 radical was generated by the photolysis of C_6H_5NO (nitrosobenzene) at 248 nm;[6−15] the conversion of C_6H_5NO at this wavelength with an unfocused, 30−50 mJ KrF laser beam was in the range 20−40% with no evidence of secondary photofragmentation of C_6H_5. The initial concentration of C_6H_5 in each experimental run was determined reproducibly from the depletion of C_6H_5NO in the presence of an excess amount of HBr diluted in He. The known fast exchange reaction,[9] $C_6H_5 + HBr \rightarrow C_6H_6 + Br$, prevents the facile recombination reaction $C_6H_5 + NO \rightarrow C_6H_5NO$[8] and other C_6H_5 radical reactions from occurring so as to give a correct calculation of the initial concentration of C_6H_5, $[C_6H_5]_0$. The typical time-resolved transient signals are shown in Figure 1. The rise of the $C_{12}H_{10}$ signal is attributable to the formation of $C_{12}H_{10}$ from the recombination reaction of C_6H_5 and the decay of C_6H_5NO signal

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TABLE 1: Typical Reaction Conditions[a] and Rate Constants[b] at Selected Temperatures Studied

T (K)	P	$[C_6H_5NO]_0$	$[NO]_0$	$[C_6H_5]_0$	$[C_{12}H_{10}]_t$[c]	$[C_6H_5NO]_t$[c]	$[C_{12}H_{10}NO]_t$[d]	k_1	k_4
300	6620	6.21	12.21	2.02	0.106	7.283	0.367	1.012	0.486
	6650	6.09	17.13	1.98	0.082	7.315	0.312	1.073	0.574
	6700	6.06	19.91	1.97	0.070	7.364	0.279	1.036	0.580
	6770	6.02	23.49	1.96	0.061	7.401	0.218	1.034	0.514
353	6620	5.68	14.28	2.51	0.183	6.880	0.473	1.145	0.548
	6620	5.59	17.54	2.48	0.158	6.934	0.405	1.187	0.558
	6620	5.52	19.88	2.45	0.143	7.027	0.327	1.186	0.492
	6620	5.43	23.07	2.41	0.132	6.985	0.295	1.269	0.520
	6620	5.37	25.41	2.38	0.118	6.956	0.277	1.257	0.540
405	6620	5.18	20.44	2.77	0.187	6.783	0.394	1.222	0.497
	6620	5.01	26.86	2.68	0.159	6.711	0.329	1.265	0.560
	6620	4.89	31.55	2.61	0.135	6.670	0.282	1.271	0.562
	6620	4.79	35.50	2.56	0.116	6.616	0.249	1.098	0.561
442	6840	5.75	15.25	2.69	0.266	7.000	0.451	1.331	0.425
	6840	5.60	20.74	2.62	0.201	7.013	0.400	1.289	0.494
	6840	5.42	27.29	2.53	0.156	6.942	0.350	1.320	0.569
	6840	5.28	32.56	2.47	0.121	6.893	0.304	1.230	0.591
	6840	5.17	36.75	2.41	0.122	6.796	0.269	1.438	0.599
500	6880	5.95	14.85	2.55	0.236	7.010	0.508	1.311	0.447
	6990	5.87	21.18	2.52	0.204	7.190	0.396	1.341	0.462
	7110	5.80	27.98	2.48	0.159	7.270	0.346	1.173	0.507
	7220	5.72	34.21	2.45	0.144	7.313	0.288	1.424	0.502
	7320	5.67	39.34	2.43	0.133	7.346	0.246	1.486	0.496

[a] The units of total pressure and all concentrations are in mTorr. $[X]_0$ represents the concentration of species X immediately after photolysis, $t = 0$. [b] k is in units of 10^{13} cm^3/(mol s). [c] The signal amplitudes were taken at $t = 10$ ms in their plateau regions. [d] The yields of biphenyl nitroxide were calculated by eq 9. See text for explanation.

indicates the depletion of C_6H_5NO by photolysis. A detailed explanation will be given later.

The rate constant for the recombination of C_6H_5 radicals was determined by measuring the absolute yields of biphenyl in the presence of varying amounts of NO, which competes with the recombination process. The absolute concentration of $C_{12}H_{10}$ and the regenerated concentration C_6H_5NO formed by the competing reactions

$$C_6H_5 + C_6H_5 \xrightarrow{1} C_{12}H_{10} \tag{1}$$

$$C_6H_5 + NO \xrightarrow{3} C_6H_5NO \tag{3}$$

can be calibrated with prepared mixtures. For $C_{12}H_{10}$, the saturated vapor pressure at room temperature (297 K) diluted with 50 Torr of He was used as the calibration sample. For C_6H_5NO, varying known amounts of the molecule were diluted with 100 Torr of He and were used as calibration mixtures after overnight mixing.

All chemicals used in the present study (C_6H_5NO, $C_{12}H_{10}$, and HBr) were obtained from Aldrich. HBr, which is known to contain H_2 impurity, was purified by trap-to-trap distillation. C_6H_5NO was purified by recrystallization using ethanol as solvent[27] with subsequent vacuum distillation to remove the solvent. The $C_{12}H_{10}$, which was determined to have 11.0 mTorr vapor pressure at 297 K, was stored in a 5 L Pyrex bulb and was degassed by prolonged diffusion pumping. He (99.999% purity) acquired from Specialty Gases was used without further purification.

Results

The experimental conditions, a set of data and kinetically modeled results, are summarized in Table 1. The results indicate that the initial concentration of C_6H_5, $[C_6H_5]_0$, determined by the depletion of C_6H_5NO in the presence of an excess amount of HBr ($[HBr]/[C_6H_5] > 300$), is always greater than the quantity $2[C_{12}H_{10}]_t + ([C_6H_5NO]_t - [C_6H_5NO]_0)$, where $[C_{12}H_{10}]_t$ and $[C_6H_5NO]_t$ are the concentrations of biphenyl and nitrosobenzene measured in the plateau region of the concentration time profiles, typically $t \geq 2$ ms. $[C_6H_5NO]_0$ is the concentration of nitrosobenzene measured after photolysis in the presence of excess HBr. Accordingly, $[C_6H_5NO]_0 + [C_6H_5]_0$ represents the concentration of nitrosobenzene before photolysis.

The apparent loss of the C_6H_5 radical at time t, as mentioned above, is attributable to the association reaction

$$C_6H_5 + C_6H_5NO \xrightarrow{4} (C_6H_5)_2NO \tag{4}$$

producing the biphenyl nitroxide radical, which had been previously detected in solution at room temperature.[28] Our search for m/z 184 indeed revealed the presence of the species, which was not present before or after photolysis in the presence of the excess amount of HBr.

In order to account for the mass balance of the C_6H_5, we write

$$\Delta[C_6H_5] = [C_6H_5]_0 - 2[C_{12}H_{10}]_t - ([C_6H_5NO]_t - [C_6H_5NO]_0) \tag{5}$$

where $\Delta[C_6H_5]$ is the disappearance of C_6H_5 through reaction 4 which consumes both C_6H_5 and C_6H_5NO (see Figure 1). Again, by mass balance,

$$[C_6H_5]_0 = 2[C_{12}H_{10}]_t + [C_6H_5NO]_{gain} + [(C_6H_5)_2NO]_t \tag{6}$$

and

$$\begin{aligned}[C_6H_5NO]_t - [C_6H_5NO]_0 &= [C_6H_5NO]_{gain} - [C_6H_5NO]_{loss} \\ &= [C_6H_5NO]_{gain} - [(C_6H_5)_2NO]_t \end{aligned} \tag{7}$$

where $[C_6H_5NO]_{gain}$ is the formation of C_6H_5NO by reaction 4 and $[C_6H_5NO]_{loss}$ is the consumption of C_6H_5NO by reaction 4. Combining eqs 6 and 7 with eq 5, and noting that $[C_6H_5NO]_{loss}$ is the same as $[(C_6H_5)_2NO]_t$, we obtain

$$\Delta[C_6H_5] = 2[(C_6H_5)_2NO]_t \tag{8}$$

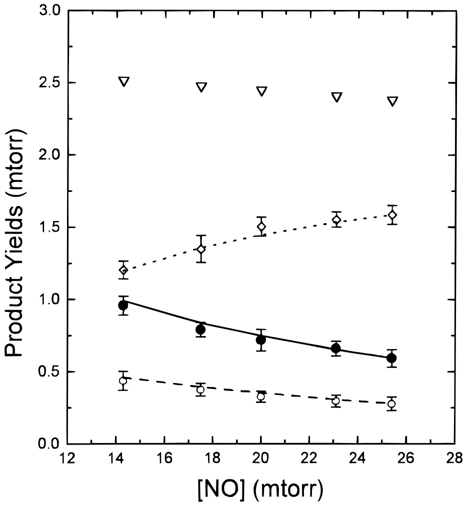

Figure 2. Concentrations of C_6H_5 and product yields as functions of NO concentration: (▽) C_6H_5, (◇) C_6H_5NO, (●) $C_{12}H_{10}$ × 5; (○) $(C_6H_5)_2NO$. Curves are kinetically modeled values.

The mass balance for C_6H_5 is then

$$[C_6H_5]_0 = 2[C_{12}H_{10}]_t + ([C_6H_5NO]_t - [C_6H_5NO]_0) + 2[(C_6H_5)_2NO]_t$$

or

$$[(C_6H_5)_2NO]_t = {}^1/_2\{[C_6H_5]_0 - 2[C_{12}H_{10}]_t - [C_6H_5NO]_t + [C_6H_5NO]_0\} \quad (9)$$

We kinetically modeled the yields of $C_{12}H_{10}$, C_6H_5NO, and $(C_6H_5)_2NO$ at time t with the following three-step mechanism:

$$C_6H_5 + C_6H_5 \xrightarrow{1} C_{12}H_{10} \quad (1)$$

$$C_6H_5 + NO \xrightarrow{3} C_6H_5NO \quad (3)$$

$$C_6H_5 + C_6H_5NO \xrightarrow{4} (C_6H_5)_2NO \quad (4)$$

by adjusting the values of k_1 and k_4 with the known rate constant for reaction 3, $k_3 = 2.7 \times 10^{12}e^{433/T}$ $cm^3/(mol\ s)$.[8] A typical set of experimental and kinetically modeled results at 355 K of the three product concentrations as functions of NO is presented in Figure 2. The experimental yields of biphenyl nitroxide were obtained by eq 9 using measured $[C_6H_5]_0$, $[C_6H_5NO]_t$, $[C_6H_5NO]_0$, and $[C_{12}H_{10}]_t$. In Figure 2, the kinetically modeled results are shown as curves, which can quantitatively depict the variation of $C_{12}H_{10}$, C_6H_5NO, and $(C_6H_5)_2NO$ with the concentration of NO using a reproducible set of k_1 and k_4 (see Table 1 also). The averaged values of k_1 and k_4 obtained from the modeling of kinetic data covering five temperatures between 300 and 500 K are graphically presented in Figure 3. A weighted least-squares analysis of the data by convoluting the reported error for k_3[8] gave for reaction 1

$$k_1 = (1.39 \pm 0.11) \times 10^{13}e^{-(56\pm33)/T} \quad cm^3/(mol\ s) \quad (10)$$

and for reaction 4

$$k_4 = (4.90 \pm 0.19) \times 10^{12}e^{(34\pm16)/T} \quad cm^3/(mol\ s) \quad (11)$$

Discussion

The rate constant for the recombination of C_6H_5 radicals presented in Figure 3 constitutes the first determination of k_1. The present result, $k_1 = 1.4 \times 10^{13}e^{-56/T}$ $cm^3/(mol\ s)$, falls within the range of values assumed, $1 \times 10^{14}-3 \times 10^{12}$ $cm^3/(mol\ s)$, over time.[16-19] The value of k_1 at 298 K, 1.2×10^{13} $cm^3/(mol\ s)$, is close to those of alkyl radical recombination reactions.[29]

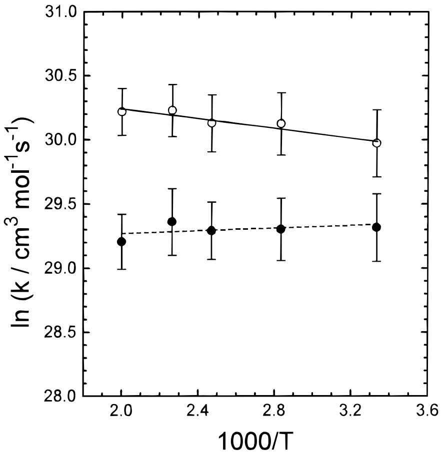

Figure 3. Arrhenius plots for the rate constants of $C_6H_5 + C_6H_5$ (○) and $C_6H_5 + C_6H_5NO$ (●) reactions.

It deserves some speculation whether the small apparent activation energy, 0.4 kcal/mol, exists. At present, the system with 12 heavy atoms defies any reasonable attempt of quantitative ab initio quantum calculations. In principle, the recombination reaction may take place by the following two paths via singlet and/or triplet potential energy surfaces:

direct association

$$C_6H_5 + C_6H_5 \rightarrow C_6H_5{\cdot\cdot}C_6H_5 \rightarrow C_6H_5{-}C_6H_5\ (C_{12}H_{10})$$

indirect association by addition−isomerization

$$C_6H_5 + C_6H_5 \rightarrow C_6H_5{\cdot}CH{=}CHCH{=}CCH{=}CH \rightarrow C_6H_5{-}CHCHCH{=}CCH{=}CH \xrightarrow{\text{H migration}} C_6H_5{-}C_6H_5\ (C_{12}H_{10})$$

The direct, singlet state association at the radical sites of C_6H_5 is expected to occur with little or no activation barrier, whereas the recombination by addition−isomerization is expected to have a small activation energy similar to that in the $C_6H_5 + C_6H_6 \rightarrow C_{12}H_{11}$ reaction, which has an apparent activation energy of 4 kcal/mol[18] (at low temperatures). Since the addition process is also quite exothermic ($\Delta H \leq -74$ kcal/mol) due to the formation of a strong C−C bond (~110 kcal/mol) at the expense of a fraction of the resonance energy (<36 kcal/mol), the internal excitation in the adduct may be sufficient to bring about the isomerization (H migration) process. A small contribution of the addition−isomerization at higher temperatures may result in the small overall activation energy observed.

Since the concentration of biphenyl was determined by calibration at the m/z 154 parent ion peak, it may be affected to some extent by the presence of biphenyl nitroxide with *m/z* 184. To our knowledge, the fragmentation pattern of $(C_6H_5)_2NO$ has not been experimentally measured. Accordingly, we could only draw the conclusion from examining its analogous compounds such as $(C_6H_5)_2NH$, $(C_6H_5)_2CO$, and $C_6H_5NN(O)C_6H_5$, whose fragmentation patterns have been determined and reported in the literature.[30] At the ionization energy employed in the present study, 70 eV, all the aforementioned compounds exhibit negligible ion abundances at *m/z* 154, typically ≤0.05 of the most abundant ions. Therefore, we assumed no contribu-

TABLE 2: Rate Constants of Several Abstraction Reactions Reevaluated with Our k_1

reaction	T (K)	log (A/cm^3/(mol s))	E_a(kcal/mol)	ref
H_2	453−623	10.63	6.7	*a*
CH_4	453−623	10.85	7.7	*a*
	550−680	11.56	11.3	*b*
i-C_4H_{10}	550−680	11.46	6.9	*b*
c-C_3H_6	583−680	11.06	8.7	*b*
$CH_3COC_6H_5$	550−680	11.26	6.5	*b*
CF_3H	453−773	9.83	5.4	*a*
C_2H_2	1000−1330	14.02	10.3	*c*
C_2H_4	1000−1330	12.82	6.4	*c*
C_6H_6	1000−1330	12.92	8.7	*c*

[a] Reference 16. [b] Reference 17; the originally reported rate constants were evaluated with $k = 1 \times 10^{14}$ cm^3/(mol s). [c] Reference 18.

tion or contamination from $(C_6H_5)_2NO$ to our biphenyl concentration measurement.

The formation of biphenyl nitroxide and the average value of the rate constant for its production, $k_4 = 5.4 \times 10^{12}$ cm^3/(mol s), appear to be reasonable. Dialkyl nitroxides are known to be stable. For example, the first C−N bond in $(CH_3)_2NO$ has been calculated to be as strong as 43 kcal/mol by Melius using the BAC-MP4 method.[31] In fact, di-(t-$C_4H_9)_2NO$ is a well-known radical trap which is commercially available and is typically delivered in bottles.[32]

The reactions of alkyl radicals with nitrosoalkanes have been investigated semiquantitatively by Lampe and co-workers[33,34] using mass spectrometry. For $CD_3 + CD_3NO$, the rate constant for the formation of dimethyl-d_6 nitroxide was reported to have a lower limit of 4×10^{12} cm^3/(mol s) at room temperature, while for $C_2H_5 + C_2H_5NO$, its lower limit was established as 1.4×10^{12} cm^3/(mol s) at 329 K. These results are consistent with our finding for $C_6H_5 + C_6H_5NO$, 5.4×10^{12} cm^3/(mol s).

Possibility of Wall Effects. At present, the possibility of wall effects on C_6H_5 kinetics cannot be quantitatively assessed. However, for these fast phenyl reactions, such effects may be negligible. For example, in our preceding paper on $NH_2 + NO$, which occurs with a rate comparable to the C_6H_5 recombination reaction, we have demonstrated that coating the reactor with concentrated phosphoric acid did not lead to measurable effects on the values of its total rate constant and H_2O−product branching ratio at pressures as low as 2 Torr.

After we completed the phenyl kinetic measurement, we have examined the possibility of wall effects on a well-studied recombination reaction, $CH_3 + CH_3$. For several reaction pressures ranging from 2 to 10 Torr with CH_3COCH_3 as the radical source and He as carrier gas, the recombination rate constant determined by the growth rate of C_2H_6 increases from 1.7×10^{13} to 2.1×10^{13} cm^3/(mol s), independent of surface coating. These pressure-dependent rate constants agree closely with the values reported by Gutman, Pilling, and co-workers.[35]

Reevaluation of Rate Constants for Several Known C_6H_5 + RH Reactions. Prior to our recent measurements of rate constants for C_6H_5 reactions with the CRD method,[6−15] about a dozen rate constants for the simple abstraction reactions

$$C_6H_5 + RH \rightarrow C_6H_6 + R$$

including $C_6H_5 + H_2$ mentioned in the Introduction were determined with reference to reaction 1, assuming a wide range of k_1 values, from 1×10^{14} to 3×10^{12} cm^3/(mol s), as alluded to earlier. In Table 2, we summarize these reactions with the reevaluated Arrhenius parameters using our present result, $k_1 = 1.4 \times 10^{13} e^{-56/T}$ cm^3/(mol s).

Some of the reactions with lower activation energies, e.g., $C_6H_5 + i$-C_4H_{10} and $CH_3COC_6H_5$, which may be amenable to kinetic measurements by CRD, will be investigated in the near future for direct comparison. For C_6H_5 reactions with C_2H_2 and C_2H_4, whose rate constants measured by Stein and collaborators above 1000 K using a Knudsen cell under low-pressure conditions,[18] have been shown to be consistent with our calculated values by the RRKM theory fitted to our low-temperature CRD data.[11,14] Because the long extrapolation covering several decades of k-values, the increase in the reference rate constant from 3×10^{12} to $1.4 \times 10^{13} e^{-56/T}$ cm^3/(mol s), amounting to about a factor of 2.4 at 1000 K, is not expected to bring about any severe disagreement from our earlier conclusion. However, this question will be examined when additional kinetic data are acquired for the two reactions at higher temperatures than have been achieved[11,14] and analyzed with the aid of high-level ab initio MO results.

Conclusions

In the present work, we have measured for the first time the rate constant for the recombination of C_6H_5 radicals using the laser photolysis/mass spectrometric technique. The absolute product yields of biphenyl and the increased formation of C_6H_5NO over that determined immediately after photolysis as functions of added NO concentrations have been carefully measured by using standard mixtures. From the analysis of mass balance, it was concluded and subsequently confirmed that an additional reaction product, biphenyl nitroxide, was formed in the reaction. Kinetic simulation of the measured yields of biphenyl, nitrosobenzene, and the calculated amounts of biphenyl nitroxide employing the known rate constant for $C_6H_5 + NO \rightarrow C_6H_5NO$ at varying NO concentrations allowed us to reproducibly obtain the rate constants for biphenyl and biphenyl nitroxide formation, respectively:

$$k_1 = (1.39 \pm 0.11) \times 10^{13} e^{-(56\pm33)/T} \quad \text{cm}^3/(\text{mol s})$$

$$k_4 = (4.90 \pm 0.19) \times 10^{12} e^{+(34\pm16)/T} \quad \text{cm}^3/(\text{mol s})$$

We have also used our result for k_1 to reevaluate the existing rate constants previously calculated with assumed, grossly different values of k_1. The new Arrhenius parameters thus obtained are summarized in Table 2 for future applications.

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