Kinetics of the Reactions of OH with C_2H_6, CH_3CCl_3, $CH_2ClCHCl_2$, $CH_2ClCClF_2$, and CH_2FCF_3

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The rate constants of the five H-abstraction reactions are measured from about 250 to 470 K by using the discharge-flow technique. Arrhenius parameters, three-parameter fits, and modified A and E values centered at 300 K are obtained. As in earlier papers on substituted methanes, $A_{\rm th}^{300}$ is calculated by thermochemical transition-state theory and compared with $A_{\rm exp}^{300}$, giving good agreement, on average, for a C–H–O bond angle of 150°. Three-parameter fits are reexamined for the ten methane reactions, their usefulness is discussed, and the dependence of $A_{\rm exp}^{300}$ on n, the temperature exponent, is calculated. Consequently, it is suggested that fitting routines be guided by theoretical considerations.

Introduction

Hydrogen abstraction by OH radicals has become the most widely widely studied class of elementary two-body processes, both for reasons of important applications in atmospheric and combustion chemistry and of comparisons with predictions by reaction rate theories. In earlier papers,[1,2] we have presented experimental data for OH reactions with CH_4 and with all nine Cl- and F-substituted methanes with an abstractable H and have compared these rate data with calculations using semiempirical transition-state theory.[3,4] In this paper, we present new rate data on C_2H_6, $CH_2ClCClF_2$, and CH_2FCF_3 along with previously published results[5] on CH_3CCl_3 and $CH_2ClCHCl_2$ in an extension of our test of that theory.

Such tests are very important as verification of the predictive power of the theory and thereby of its limitations when it is used to make ab initio estimates of rate parameters. In the hierarchy of theoretical treatments of elementary rate processes ranging from ab initio quantum-chemical calculations to semiempirical thermochemical kinetics, it is particularly important to have a rough estimate of the probable errors of calculated rate parameters.

Our earlier comparison[2] dealt only with the Arrhenius A values of the ten methane H atom abstraction reactions, since neither the semiempirical theory nor the more rigorous ab *initio* quantum-chemical theory is able to calculate energy barriers to better than ±1 to 2 kcal mol^{-1}, corresponding to factors of 5–30 up or down (nearly 3 orders of magnitude range) in the rate constants at 298 K. The results were encouraging, on average, but disappointing in detail. For reasonable assumptions of the geometries of the R–H–OH transition states for the ten reactions, the average value of $A_{\rm th}/A_{\rm exp}$ at 300 K was about 1.2, well within the expected range, but the individual ratios deviated strongly from that mean, in a way that could not be rationalized on the basis of physical parameters such as bond energies, dipole moments, or van der Waals interactions.

The five ethane reactions discussed in this paper represent a much smaller, more incomplete set. Their rate constants were measured in the same way by using the discharge-flow method, and their preexponential factors, $A_{\rm exp}^{300}$, were adjusted to T = 300 K via three-parameter fits of the data and compared with theoretical estimates based on thermochemical transition-state theory[3,4] as before.[1,2] The usefulness and meaning of such three-parameter fits are examined in detail in the Appendix.

Experimental Section

The discharge-flow, resonance fluorescence apparatus was described earlier. The 90-cm-long reaction section of the 170-cm-long 2.54-cm-i.d. flow tube was temperature controlled to about ±1 K. The OH microwave discharge lamp, grating monochromator, and photomultiplier detector allowed OH detection at concentrations of about 2×10^9 cm^{-3} for $S/N = 1$. Stable reactants were added through a movable injector of 230-cm length and 0.3-cm o.d. OH was generated by the H + NO_2 reaction using a slight excess of NO_2. The flow tube surface was coated with H_3PO_4 and baked at 450 K to reduce the effective surface rate constants, $k_{\rm W}$, of OH to about 15–20 s^{-1} near 300 K. For all details of the experimental procedure and data analysis, the reader is referred to the earlier paper.[1]

Reactant Purifications. C_2H_6 (Matheson, research grade, 99.96% purity) was used without further purification.

CH_3CCl_3 was purified extensively as described earlier.[5] Gas chromatographic analysis indicated better than 99.999% purity.

$CH_2ClCHCl_2$ reacts about 30 times faster with OH than CH_3CCl_3. Following purification, it was analyzed to be better than 99.9% pure.[5]

Highly purified samples of $CH_2ClCClF_2$ (CFC 132B) and CH_2FCF_3 (CFC 134A) were obtained from Allied Chemical Corp., the former better than 99.999% pure and the latter better than 99.9% pure.

Experimental Results

Table I shows the measured rate constants for the five reactions over temperature ranges from 250–270 to 460–470 K. These temperature ranges were covered with 5–11 different temperature measurements, and each individual rate constant was obtained from a least-squares fit of k^1 vs. [RH] at 6–10 concentrations of RH. Figure 1 shows the Arrhenius diagrams for the five reactions. Table II lists Arrhenius A and E values, three-parameter fits in the form $C(T/300)^n \exp(-E'/RT + E'/300R)$, and A^{300} and E^{300} values calculated from the three-parameter expression. The fitting procedure, error analysis, and a review of our earlier methanes data[1] are presented in the Appendix.

Comparison with Published Data

$OH + C_2H_6$. Six room-temperature measurements by direct methods have been reported.[6-11] Adjusted to T = 298 K, the rate constants are, in units of 10^{-13} cm^3 $molecule^{-1}$ s^{-1}, 2.8 ± 0.6,[6] 2.7 ± 0.2,[7] 3.0 ± 0.6,[8] 2.6 ± 0.4,[9], 2.4 ± 0.4,[10] and 2.6 ± 0.2[11] compared to our 3.1 ± 0.3, where the uncertainties represent 1σ, but do not always include estimates of experimental errors. Neither flash photolysis nor discharge-flow measurements are

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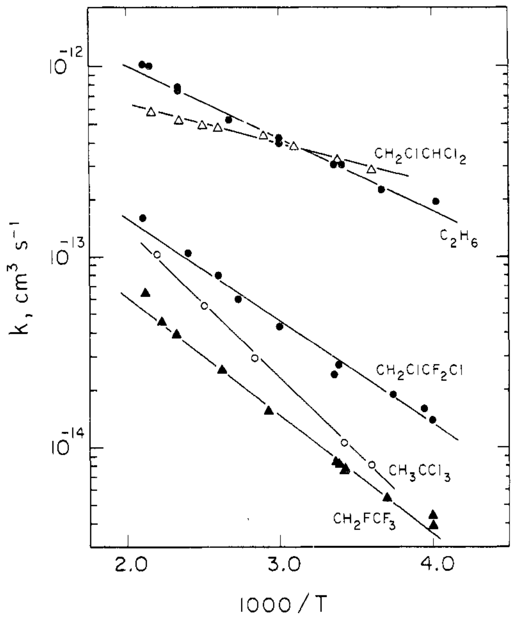

Figure 1. Arrhenius diagram for five OH + RH reactions.

likely to have absolute accuracies much better than ±10%, so that the above agreement is satisfactory.

Two earlier studies have included temperature dependence. Greiner[6] reported Arrhenius parameters of $(1.9 \pm 0.3) \times 10^{-11}$ cm^3 s^{-1} and 2.45 ± 0.11 kcal mol^{-1} over the range 297–493 K. Tully et al.[11] report $A = (2.17 \pm 0.57) \times 10^{-11}$ cm^3 s^{-1} and $E = 2.62 \pm 0.19$ kcal mol^{-1} from 295 to 500 K and a three-parameter expression $1.43 \times 10^{-14}T^{1.05} \exp(-911/T)$ from 297 to 800 K, whereas we find $(6.11 \pm 0.60) \times 10^{-12}$ and 1.76 ± 0.07 and a three-parameter expression $3.90 \times 10^{-21}T^{3.09} \exp(+169/T)$ over the range 248–472 K. Reduced to two-parameter Arrhenius expressions centered at 300 K, the corresponding A_{exp}^{300} and E_{exp}^{300} values are 1.63×10^{-11} cm^3 s^{-1} and 2.44 kcal mol^{-1} for Tully et al.[11] vs. our 3.87×10^{-12} and 1.57. These expressions reduce to virtually identical k^{300} values of 2.72×10^{-13} and 2.78×10^{-13}, respectively, but ours report a lower activation energy as well as larger curvature and therefore a lower effective A value at 300 K near the low end of the experimental T range. Cohen's theoretical extrapolation[12] gives the three-parameter expression $1.29 \times 10^{-17}T^{2.0} \exp(-430/T)$ roughly midway between the other two, $A^{300} = 8.6 \times 10^{-12}$ cm^3 s^{-1}, $E^{300} = 2.05$ kcal mol^{-1}, and $k^{300} = 2.75 \times 10^{-13}$ cm^3 s^{-1}. This large range of Arrhenius parameters will be discussed further below and in the Appendix. A recent study of the OH + C_2H_6 reaction by competitive photolysis[13] from 403 to 683 K using OH + CO as a reference reaction is in general agreement with other data. No Arrhenius parameters were reported.

OH + CH_3CCl_3. As our earlier paper[5] and that of Kurylo et al.[14] have shown, the reason for discrepancies with previously published rate parameters at room temperature and, especially, at lower temperatures had to do with reactant purity, i.e. small amounts of olefinic impurities had not been fully removed in these previous studies. The present comparison, therefore, only includes the results of Kurylo et al.,[14] who reported $A = (5.41 \pm 0.92) \times 10^{-12}$ cm^3 s^{-1} and $E = 3.60 \pm 0.09$ kcal mol^{-1} (1σ uncertainties), in very good agreement with our $(5.03 \pm 1.19) \times 10^{-12}$ and 3.57 ± 0.15. Our three-parameter expression, $5.95 \times 10^{-20}T^{2.65} \exp(-858/T)$, reduces to $A_{\text{exp}}^{300} = 3.09 \times 10^{-12}$ cm^3 s^{-1} and $E_{\text{exp}}^{300} = 3.29$ kcal mol^{-1} and to $k^{300} = 1.26 \times 10^{-14}$ cm^3 s^{-1}. As in the case of ethane, the fairly strong curvature of the Arrhenius plot results in a decrease from the overall A to A_{exp}^{300}.

TABLE I: Rate Constant Data for Reactions of OH with C_2H_6 and Four Substituted Ethanes

reactant	T, K	$10^{13}k$, cm^3 s^{-1}	conc range × 10^{-14}, cm^{-3}
C_2H_6	248	1.96 ± 0.13[a]	5.9–30.4
	273	2.28 ± 0.14	5.2–33.8
	294	3.10 ± 0.20	3.8–26.4
	298	3.06 ± 0.21	5.7–26.7
	333	4.26 ± 0.27	3.9–24.4
	333	4.03 ± 0.27	4.4–29.0
	375	5.38 ± 0.35	4.2–15.8
	375	5.29 ± 0.34	5.1–19.0
	428	7.99 ± 0.54	2.6–12.2
	429	7.70 ± 0.48	2.6–16.4
	464	9.93 ± 0.68	2.6–13.4
	472	10.3 ± 0.67	3.1–13.7
CH_3CCl_3	278	0.083 ± 0.007	6.2–37.5
	293	0.106 ± 0.011	7.0–38.1
	352	0.293 ± 0.019	6.0–25.6
	400	0.552 ± 0.041	3.5–17.5
	457	1.02 ± 0.065	3.05–9.3
$CH_2ClCHCl_2$	277	2.84 ± 0.21	0.33–2.92
	295	3.18 ± 0.20	0.38–2.52
	322	3.76 ± 0.23	0.13–2.43
	346	4.36 ± 0.28	0.21–2.01
	386	4.68 ± 0.29	0.21–2.19
	400	4.92 ± 0.31	0.27–1.82
	424	5.27 ± 0.35	0.23–1.54
	461	5.76 ± 0.37	0.25–1.95
CH_2ClCF_2Cl	249	0.142 ± 0.011	2.3–24.4
	253	0.160 ± 0.010	5.7–23.0
	267	0.191 ± 0.016	4.3–21.6
	295	0.272 ± 0.018	3.5–23.7
	297	0.242 ± 0.016	6.4–23.1
	333	0.431 ± 0.028	2.1–17.0
	365	0.595 ± 0.037	3.3–15.7
	383	0.806 ± 0.051	1.6–9.6
	418	1.04 ± 0.065	1.5–10.1
	473	1.60 ± 0.115	1.7–7.0
CH_2FCF_3	249	0.0393 ± 0.0024	10.4–116
	250	0.0441 ± 0.0040	15.1–102
	268	0.0552 ± 0.0035	15.0–88
	291	0.0773 ± 0.0071	8.4–90.7
	295	0.0823 ± 0.0055	12.1–73.8
	298	0.0844 ± 0.0073	10.2–60.6
	342	0.154 ± 0.012	6.2–43.1
	380	0.254 ± 0.017	4.2–36.0
	430	0.394 ± 0.026	3.7–25.8
	447	0.456 ± 0.029	2.8–27.9
	473	0.644 ± 0.040	2.7–19.0

[a] Error limits are 1σ including estimates of experimental errors (see ref 1).

OH + $CH_2ClCHCl_2$. No other study of this reaction seems to have been published. Our data are shown in Tables I and II. The small temperature dependence, $E = 0.96$ kcal mol^{-1}, the negative n, and its very large uncertainty throw doubt on the usefulness of this three-parameter expression. However, the derived $A_{\text{exp}}^{300} = 2.04 \times 10^{-12}$ differs little from the $A = 1.65 \times 10^{-12}$ of the simple Arrhenius fit.

OH + $CH_2ClCClF_2$. No other results are available. Our data show strong Arrhenius curvature. The three-parameter expression. $5.54 \times 10^{-26}T^{-4.58} \exp(+252/T)$, reduces to $A_{\text{exp}}^{300} = 1.20 \times 10^{-12}$ cm^3 s^{-1}, $E_{\text{exp}}^{300} = 2.23$ kcal mol^{-1}, and $k^{300} = 2.8 \times 10^{-14}$ cm^3 s^{-1}. The A_{exp}^{300} value is 40% lower than the two-parameter value of $A = 2.02 \times 10^{-12}$ cm^3 s^{-1}. As is discussed in the Appendix, large temperature exponents, n, in three-parameter expressions, obtained over limited temperature ranges, are of doubtful significance, and one may be better advised to be guided by theoretical considerations. For an assumed $n = 2.0$, $A_{\text{exp}}^{300} = 1.31 \times 10^{-12}$ cm^3 s^{-1}.

OH + CH_2FCF_3. Watson[15] quotes Arrhenius parameters of 1.87×10^{-12} cm^3 s^{-1} and $E = 2.68 \pm 0.16$ kcal mol^{-1} over the range

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TABLE II: Arrhenius Parameters, Three-Parameter Fits,[a] and Modified Arrhenius Parameters for OH + RH Reactions

RH	$10^{12}A$, cm^3 s^{-1}	E, kcal mol^{-1}	$10^{14}C$, cm^3 s^{-1}	n	E', kcal mol^{-1}	$10^{12} \times A_{exp}^{300}$, cm^3 s^{-1}	E_{exp}^{300}, kcal mol^{-1}
C_2H_6	6.11 ± 0.60	1.76 ± 0.07	30.9 ± 0.8	3.09 ± 1.01	−0.34 ± 0.68	3.87	1.51
CH_3CCl_3	5.04 ± 0.96	3.57 ± 0.13	1.25 ± 0.06	2.65 ± 2.44	1.70 ± 1.72	3.09	3.29
$CH_2ClCHCl_2$	1.65 ± 0.27	0.96 ± 0.11	33.2 ± 1.1	−1.21 ± 1.91	1.80 ± 1.34	2.04	1.08
CH_2ClCCl_2F	2.02 ± 0.24	2.51 ± 0.07	2.84 ± 0.08	4.58 ± 1.13	−0.50 ± 0.75	1.20	2.23
CH_2FCF_3	1.10 ± 0.11	2.83 ± 0.07	0.894 ± 0.029	4.36 ± 1.14	−0.09 ± 0.77	0.60	2.51

[a] $k \equiv C(T/300)^n \exp(-E'/RT + E'/300R) \equiv BT^n \exp(-E'/RT)$ where $B \equiv C300^{-n} \exp(E'/300R)$. Therefore, $A_{exp}^{300} \equiv C \exp(n + E'/300R)$, and $E_{exp}^{300} = E' + 300nR$.

TABLE III: Calculations of $\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1}) and A_{th}^{300} (10^{-12} cm^3 s^{-1}) via Model Reaction and Comparison with A_{exp}^{300}

	RH					
	C_2H_6	CH_3CCl_3	$CH_2ClCHCl_2$		CH_2ClCCl_2F	CH_2FCF_3
$\Delta S^{\ddagger}$ (model)	−31.3	−33.1	−35.4	−37.2	−35.7	−36.8
spin	1.4	1.4	1.4	1.4	1.4	1.4
ext rot (150°)	1.8	0.8	0.7	0.7	0.8	0.9
ext rot (180°)	1.7	0.5	0.6	0.6	0.6	0.8
int rot (150°)	3.1	3.9	4.2	4.4	3.9	3.6
int rot (180°)	0.3	0.6	0.9	1.1	0.6	0.4
1 O-H-C (150°)	0.7	0.7	0.7	0.7	0.7	0.7
2 O-H-C (180°)	1.4	1.4	1.4	1.4	1.4	1.4
OC → rx coord	−0.1	−0.1	−0.1	−0.1	−0.1	−0.1
HOC → HO-H-C	0.1	0.1	0.1	0.1	0.1	0.1
OCH → (O-H)-CH	0.2	0.2	0.1		0.1	0.1
OCX → (O-H)-CX			0.7	1.2	0.7	0.7
CCO → CC-H	−0.8	−0.8	−0.8	−0.8	−0.8	−0.8
$\Delta S^{\ddagger}$(150°)	−24.9	−26.9	−28.4	−29.6	−28.9	−30.2
A_{th}^{300}(150°)	6.93	2.53	1.19	0.651	0.926	0.481
(corr A^W)	6.65	2.38	1.14	0.625	0.88	0.452
A_{th}^{300}(150°,corr)/A_{exp}^{300}	1.71	0.77	(0.57)	(0.31)	0.73	0.75
$\Delta S^{\ddagger}$(180°)	−26.8	−29.8	−31.1	−32.3	−31.7	−32.8
A_{th}^{300}(180°,corr)/A_{exp}^{300}	0.65	0.18	0.15	0.08	0.18	0.20

250–350 K, in fairly poor agreement with our 1.1×10^{-12} and 2.83 or with the derived A_{exp}^{300} and E_{exp}^{300} values of 0.60×10^{-12} and 2.51 ($n = 4.36$); i.e., our room-temperature rate constant is 2.4 times smaller than the quoted but unpublished report suggests. Clyne and Holt[16] reported rate constants from 294 to 429 K measured by a similar experimental method. Their results are somewhat scattered; for example, their extrapolated k^{298} is $(6.9 \pm 0.9) \times 10^{-15}$ cm^3 s^{-1}, in moderate agreement with out 8.4×10^{-15}, but their measured k^{294} is $(5.5 \pm 0.7) \times 10^{-15}$ cm^3 s^{-1}. Their Arrhenius parameters, $A = (3.2 \pm ^{2.3}_{1.3}) \times 10^{-12}$ cm^3 s^{-1} and $E = 3.6 \pm 0.4$ kcal mol^{-1} are larger than our $A = (1.1 \pm 0.11) \times 10^{-12}$ cm^3 s^{-1} and $E = 2.83 \pm 0.07$ kcal mol^{-1}, yet this cannot be ascribed to Arrhenius plot curvature, since their smaller temperature range is centered around the same temperature as our larger one. The large discrepancy of our room-temperature value with Martin and Paraskevopoulos's[17] recent flash photolysis value of $(5.1 \pm 0.6) \times 10^{-15}$ cm^3 s^{-1} at 298 K is difficult to understand. For four other compounds, CH_4, C_2H_6, CH_3F, and CH_2F_2, the differences between our k^{298} and theirs are +24%, +17%, −27%, and −5%, yet for CH_2FCF_3 it is +65%, far outside the combined uncertainty limits. Reactant purity cannot be invoked as a possible explanation, since the purity of our sample was >99.9% and since two of our kinetic experiments (at 268 and 295 K) used samples that had been additionally purified yet gave very similar rate constants. For an assumed $n = 2.0$, $A_{exp}^{300} = 0.72 \times 10^{-12}$ cm^3 s^{-1}, based on our data.

Theoretical Calculation and Discussion

The semiempirical transition-state calculations closely follow those of our earlier paper.[2] The A_{th}^{300} values are obtained from reference entropies of the corresponding alcohols corrected for spin, external and internal rotation, and vibration frequencies of the transition state, whose geometry is assumed to have either 180° (collinear) or 150° C–H–O geometry and partial bond extensions of 0.3 Å.

The reference or model compound entropies of the haloethanols are estimated by analogy arguments, using Benson's group additivity method, i.e. method 3 in Table I or our earlier paper.[2] For example, for CH_3CCl_3, the reference compound is CH_2OHCCl_3, and its entropy is calculated as $S°(CH_2FCCl_3) + S°(CH_3CH_2OH) - S°(CH_3CH_2F) = 88.0$ eu. The ΔS_{ref}^{*} values listed in the first row of Table III, $\Delta S_{ref}^{*} = S_{ref}° - S°(RH) - S°(OH)$, are corrected for spin, external and internal rotation, and vibration frequency changes as indicated. The treatment parallels that of the earlier paper.[2] The bond extensions of O–H and C–H are taken to be 0.3 Å each, and two C–H–O bond angles, 150 and 180°, are assumed.

For 1,1,2-trichloroethanes, there are two different abstractable H atoms and, therefore, two sets of reference compounds, entropies, and correction factors. Since reaction path degeneracy is implicitly included in the calculation, the relative contribution of the two calculated A values should be weighted by the E values of the two routes, i.e. by $\exp(-E/RT)$. These are unfortunately not known, but since the experimental activation energy is very low, the two E's are assumed to be equal, and the arithmetic mean of the calculated A values is compared with A_{exp}^{300}.

Tunneling corrections are applied following Table VI of ref 2, i.e. based on the Wigner transmission coefficient with the imaginary crossing frequency, ν^*(i cm^{-1}), based on analogy with those listed in that table. Although quantum effects have recently been incorporated in generalized transition-state theory[18] taking account of reaction path curvature, such calculations require information on potential energy surfaces that is unavailable. Furthermore, the energy barriers of these reactions are quite small and the tunneling corrections presumably also small. Their effect is, in

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TABLE IV: Arrhenius Parameters, Three-Parameter Fits, and Modified Arrhenius Parameters for OH + RH Reactions

RH	$10^{12}A$, cm^3 s^{-1}	E, kcal mol^{-1}	$10^{14}C$, cm^3 s^{-1}	n	E', kcal mol^{-1}	$10^{12}A_{\text{exp}}^{300}$, cm^3 s^{-1}	E_{exp}^{300}, kcal mol^{-1}
CH_4	5.26 ± 0.88	3.81 ± 0.12	0.85 ± 0.04	4.23 ± 2.15	0.90 ± 1.54	2.64	3.42
CH_3Cl	3.04 ± 0.43	2.51 ± 0.09	4.36 ± 0.17	3.08 ± 1.26	0.46 ± 0.84	2.04	2.29
CH_3F	8.11 ± 1.35	3.75 ± 0.12	1.59 ± 0.08	4.32 ± 1.95	0.55 ± 1.45	3.01	3.13
CH_2Cl_2	5.57 ± 0.77	2.07 ± 0.09	16.9 ± 0.6	2.54 ± 1.40	0.37 ± 0.98	3.97	1.88
CH_2ClF	2.37 ± 0.29	2.26 ± 0.08	5.25 ± 0.17	2.41 ± 1.11	0.61 ± 0.76	1.63	2.05
CH_2F_2	4.37 ± 0.58	3.51 ± 0.10	1.18 ± 0.05	3.09 ± 1.32	1.35 ± 0.91	2.51	3.19
$CHCl_3$	5.63 ± 0.68	2.35 ± 0.09	10.6 ± 0.4	2.65 ± 1.13	0.52 ± 0.79	3.57	2.10
$CHCl_2F$	1.19 ± 0.15	2.09 ± 0.09	3.52 ± 0.12	1.94 ± 1.20	0.76 ± 0.82	0.88	1.92
$CHClF_2$	1.27 ± 0.21	3.30 ± 0.12	0.53 ± 0.03	5.11 ± 2.09	−0.50 ± 1.55	0.38	2.55
CHF_3	2.98 ± 1.07	5.78 ± 0.31		(2.0)[a]		(1.44)	(5.26)

[a] $n = 2.0$ is assumed; $A_{\text{exp}}^{300} \equiv C \exp(n + E'/300R)$, and $E_{\text{exp}}^{300} = E' + 300nR$.

all cases, to lower the A value. On the basis of earlier BEBO calculations,[2] we estimate classical barrier heights of 3.1–5.4 kcal mol^{-1} for the five transition states and correction factors of 0.94–0.96 for A^{w}, the Wigner preexponential factor. More theoretical work is clearly needed for polyatomic systems to establish the importance of tunneling corrections.

The two ratios, $A_{\text{th}}^{300}(150,\text{corr})/A_{\text{exp}}^{300}$ and $A_{\text{th}}^{300}(180,\text{corr})/A_{\text{exp}}^{300}$, which represent the present extension of this test of thermochemical transition-state theory are shown at and near the bottom of Table III. The results are very similar to those of the methanes.[2] The bent transition-state geometry is clearly preferred, the average for the 150° ratio being 0.88 ± 0.48 whereas that for the linear configuration is 0.27 ± 0.22. The scatter around the mean is again large and bears no simple relation to the structure or other physical parameters of the admittedly small set of compounds.

As Table II shows, the temperature exponents, n, of the fully converged three-parameter fits are highly variable and physically probably not very significant. It is of interest, therefore, to examine how great the dependence of these ratios is on n, i.e. how strongly A_{exp}^{300} varies with n. This is taken up in some detail in the Appendix, but here we report the A_{exp}^{300} values for the choice $n = 2$ for all RH except $CH_2ClCHCl_2$ whose temperature dependence is so small that $n = 0$ is chosen. The dependence is quite weak. For C_2H_6, A_{exp}^{300} increases from 3.9 to 4.2 as n is decreased from 3.09 to 2.0; for CH_3CCl_3, it increases from 3.1 to 3.37 when n is decreased from 2.65 to 2.0; for $CH_2ClCHCl_2$, it decreases from 2.0 to 1.7 as n is increased from −1.21 to zero; for $CH_2ClCClF_2$, it increases from 1.20 to 1.31 as n is decreased from 4.58 to 2.0; and for CH_2FCF_3, it increases from 0.60 to 0.72 as n is decreased from 4.36 to 2.0. The corresponding A ratios for the 150° configuration would be 1.58, 0.71, 0.52, 0.67, and 0.63, and their average, 0.82 ± 0.43, only slightly changed from the value of 0.88 ± 0.48 given above. This is not to suggest that the three-parameter correction for $A_{\text{ex+}}$ is without effect but that its effect becomes smaller with increasing n. If the two-parameter Arrhenius A values are used without correction, the ratios become 1.09, 0.48, 0.52, 0.44, and 0.41, and their average, 0.59 ± 0.28, is lowered substantially.

It is interesting to note that a surprisingly large discrepancy exists between the corrected A_{exp}^{300} values for the C_2H_6 reaction, as stated above, i.e. 1.63×10^{-11} (ref 11) and 8.6×10^{-12} (ref 12) vs. our 3.9×10^{-12} cm^3 s^{-1}, and that our 4.2×10^{-12} for an assumed $n = 2$, which is the same n used in Cohen's fit, is still only half as large as his. If we took $n = 1.05$ to compare with Tully et al.,[11] our A_{exp}^{300} would rise only to 4.9×10^{-12}, a factor of 3.3 smaller than theirs. This is because our temperature dependence is weaker than theirs, a matter that requires more experimental work. If we adopt Cohen's A_{exp}^{300} of 8.6×10^{-12}, the A ratio for C_2H_6 drops to 0.77, and four of the five ratios (excepting only $CH_2ClCHCl_2$ with two nonequivalent H sites) become essentially identical.

Our general conclusions are similar to those of the earlier study:[2] Thermochemical transition-state theory provides a satisfactory, ab initio account of the pseudodynamical features of simple, direct atom-transfer reactions of polyatomics with small energy barriers and exothermicities. However, even in such simple applications, it does not provide reliable fine structure; i.e., it does not predict substituent effects to better than factor of 2 accuracy. The important question of tunneling corrections is still unresolved and awaits both experimental and theoretical work on carefully chosen test cases.

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Appendix

The use and limitations of three-parameter fits and corrected Arrhenius parameters is discussed here in the context of the present work and of the earlier data on the methanes.[1] Unfortunately, the nonlinear least-squares program used in the earlier paper had not converged, and the three-parameter expressions as well as the derived A^{300} and E^{300} values listed in Table II of ref 1 are incorrect. Three typing errors should also be mentioned in the data of Table I of ref 1: The lowest temperature for CH_4 was 269 K, not 278 K; the rate constant for CH_3F at 480 K was 17.1, not 16.0×10^{-14} cm^3 s^{-1}, and that for CHF_3 at 465 K was 0.564, not 0.546×10^{-14} cm^3 s^{-1}.

Table IV is the equivalent of Table II of ref 1; it lists the values of Arrhenius parameters, three-parameter fits, and the A^{300} and E^{300} values. For ease of computation, three-parameter fits are in the form $k(T) = C(T/300)^n \exp(-E'/RT + E'/300R)$, which reduces to the form $BT^n \exp(-E'/RT)$ by the transformation $B = C300^{-n} \exp(E'/300R)$ and has the advantage of the small range of C, the parametrized k^{300}, vs. the very large range of B. The other two parameters are identical in both representations.

A nonlinear least-squares computer program based on Marquardt's[19] algorithm was used for both the two- and three-parameter fits. This algorithm, described by Bevington,[20] combines a gradient search and Taylor series expansion to minimize χ^2. Bevington's implementation was modified to include an estimate of the curvature in χ^2 to obtain uncertainty limits, σ_{para}, for each parameter via $\sigma_{\text{para}} = 2[\partial^2(\chi^2)/\partial(\text{para})^2]$. We are grateful to Dr. P. E. Siska for providing the program. The uncertainties in the rate constants listed in Table I of ref 1 were used as weights in the nonlinear routine. These uncertainties include estimates of experimental variables and are in the range of 6–8% at the single standard deviation level. The calculated results for the methanes in Table IV are exactly equivalent to those for the ethanes in Table II.

The fully converged three-parameter fits differ substantially from the earlier ones for about half the compounds. The error had arisen due to the slow convergence of the earlier program which was started with a trial value of the exponent, n, in the vicinity of 2.0 and which stopped after insufficient iteration. The correct n values in Table IV show the pitfalls and uncertainties of three-parameter fits using a fairly small (six to eight) set of temperature points over a moderate range. Clearly, the largest

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(20) Bevington, P. R. "Data Reduction and Error Analysis for the Physical Sciences"; McGraw-Hill: New York, 1969; pp 235–245.

n values of 4.2–5.1 are both physically unreasonable and very uncertain, i.e. $\sigma_n \simeq \pm 2$. They should not, of course, be used outside the experimental range.

For their present purpose, i.e. the calculation of comparable, equivalent A values at a reference $T = 300$ K, they do serve a mildly useful function. Since the experimental temperature ranges extend much farther above 300 K than below it, the simple Arrhenius A value will be larger than A^{300} if there is upward rising curvature in the log k vs. $1/T$ plot. For simple, tight transition states, such curvature is usually observed, as, for example, in Cohen's[12] OH + alkanes study where n was found to range from 1.6 to 3.0 for 12 alkanes. If the A_{exp}^{300} values of Table IV are used, the $A_{\mathrm{th}}^{300}/A_{\mathrm{exp}}^{300}$ ratios of Table VII, ref 2, rise from 1.14 ± 0.71 to 1.59 ± 1.19 for the 150° angle and from 1.22 ± 0.76 to 1.71 ± 1.29 for the 165° angle, i.e. 40% on average. Considering the many large n in Table IV, this seems a relatively small change due to the mutual compensation of n and E' effects with increasing n.

In order to examine this further, modified two-parameter computer fits were calculated for fixed n rising from 0 (Arrhenius) to 5 to 7 in 0.25 increments, and the variance of the fit as well as the A_{exp}^{300} value was also calculated at each n. Although this was done for all ten methanes and five ethanes, a single example will suffice. For CH_2FCF_3 (see Table II), A_{exp}^{300} decreased from 1.10 ($n = 0$) to 0.88 ($n = 1$), 0.72 ($n = 2$), 0.63 ($n = 3$), and 0.59 ($n = 4$) and increased again to 0.61 ($n = 5$), 0.67 ($n = 6$), and 0.75 ($n = 7$). The variance of the fit came to a shallow minimum near $n = 4.25$ and then rose steeply (the full three-parameter fit gave $n = 4.36 \pm 1.14$). It is important to note that in *all* cases A_{exp}^{300} decreased fairly sharply from $n = 0$ to 2 and then less sharply at higher n values.

Two conclusions may be drawn: (1) Arrhenius plot curvature (in the form of a T^n term) cannot be determined with good accuracy except with highly accurate rate constant measurements over wide temperature ranges; (2) Modified Arrhenius parameters (i.e. local tangents to the curved plots) depend fairly weakly on n, provided, of course, that the reference temperature (e.g. 300 K) is well within the experimental range. It seems obvious, for example, that for a reference temperature, T_{M}, in the exact middle of the range, the $A_{\mathrm{exp}}^{T_{\mathrm{M}}}$ values will be nearly independent of n, whereas above T_{M} they will rise with rising n and below T_{M} they will fall (as is seen in our results).

The important suggestion by Cvetanovic et al.[21] in their excellent paper on error analysis needs to be repeated: Three-parameter fits might best be guided by theoretical considerations, not by rigid adherence to numerical analysis (ref 19, p 60). In that sense, the erroneous earlier n values near 2.0[1] are fortuitously more useful than those of Table IV, and the qualitative conclusions of our earlier papers[1,2] should stand.

If $n = 2$ is also chosen for the five ethanes, the A_{exp}^{300} values rise to 4.22 (C_2H_6), 3.37 (CH_3CCl_3), 1.33 ($CH_2ClCHCl_2$), 1.31 ($CH_2ClCClF_2$), and 0.72 × 10^{-12} cm^3 s^{-1} (CH_2FCF_3). The $A_{\mathrm{th}}^{300}/A_{\mathrm{exp}}^{300}$ ratios would change to 1.58 (C_2H_6), 0.71 (CH_3CCl_3), 0.66 ($CH_2ClCHCl_2$), 0.67 (CH_2ClCCl_2F), and 0.63 (CH_2FCF_3), not very different from those given in Table III, all for the C–H–O angle of 150°.

Registry No. CH_4, 74-82-8; CH_3Cl, 74-87-3; CH_3F, 593-53-3; CH_2Cl_2, 75-09-2; CH_2ClF, 593-70-4; CH_2F_2, 75-10-5; $CHCl_3$, 67-66-3; $CHCl_2F$, 75-43-4; $CHClF_2$, 75-45-6; CHF_3, 75-46-7; CH_3CH_3, 74-84-0; CH_3CCl_3, 71-55-6; $CH_2ClCHCl_2$, 79-00-5; CH_2ClCCl_2F, 811-95-0; CH_2FCF_3, 811-97-2; hydroxyl radical, 3352-57-6; hydrogen, 1333-74-0.

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Self-Association of Phosphinic Acids in Nonpolar Solvents. The Origin of the Apparent Dipole Moment in Symmetric Dimers

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The self-association behavior of di-*tert*-butylphosphinic acid, $(t\text{-}C_4H_9)_2P(O)OH$, and diphenylphosphinic acid, $Ph_2P(O)OH$, in benzene and 1,4-dioxane was studied by using the techniques of dielectric polarization, infrared spectroscopy, and freezing point depression. $(t\text{-}C_4H_9)_2P(O)OH$ is found to exist only as a cyclic dimer in both solvents while $Ph_2P(O)OH$ exists as a monomer–dioxane complex in dioxane and as a single self-associated species of undetermined degree of polymerization in benzene. The difference in the solution behavior of the compounds is a result of the stronger hydrogen bonds and of the steric requirements of the *tert*-butyl groups in $(t\text{-}C_4H_9)_2P(O)OH$. Because the cyclic dimer species is the only observable $(t\text{-}C_4H_9)_2P(O)OH$ structure in solution in the concentration range studied, the apparent dipole moments of 1.281 ± 0.002 D in benzene and 1.382 ± 0.008 D in 1,4-dioxane have been attributed to atomic polarization rather than a permanent dipole moment in the molecule. The dipole moment of the hydrogen-bonded monomer–dioxane complex of $Ph_2P(O)OH$ is 2.57 ± 0.02 D. Calculations of the dipole moment for various conformations of a phosphinic acid monomer, including free rotation of the OH about the P–O bond, indicate that $Ph_2P(O)OH$ in the monomer–dioxane complex has the cis conformation. This apparently results from the steric requirements of the hydrogen-bonded solvent molecule and of the phenyl groups.

Introduction

The self-association behavior of di-*tert*-butylphosphinic acid, $[(CH_3)_3C]_2P(O)OH$, and diphenylphosphinic acid, $(C_6H_5)_2P(O)OH$, in nonpolar solvents has been investigated as part of a continuing study of intermolecular hydrogen bonding. These molecules contain both hydrogen-bond acceptor and donor sites and therefore are capable of forming both cyclic and open-chain aggregates. Previous studies of other molecules having the same donor and acceptor site geometry (such as 2-pyrrolidinone,[1,2] 7-azaindole,[3] and carboxylic acids[4,5]) have shown that a cyclic dimer held together by an eight-membered hydrogen-bonded ring is a frequently occurring species in dilute solutions of nonpolar solvents. The cyclic dimer structure for a phosphinic acid is represented by

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