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Abstract

The pressure dependence of absolute rate constants for the reaction of OH + $C_2H_2 \rightarrow$ products has been examined at five temperatures ranging from 228 to 413 K. The experimental technique which was used is flash photolysis-resonance fluorescence (FP-RF). OH was produced by water photolysis and hydroxyl resonance fluorescent photons were measured by multiscaling techniques.

The results indicate that the low pressure bimolecular rate constant is $\sim 4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} over the temperature range studied. A substantial increase in the bimolecular rate constant with an increase in pressure was observed at all temperatures except 228 K. This indicates the importance of initial adduct formation and subsequent stablization. The high pressure results are well represented by the Arrhenius expression $(k_{bi})_\infty$ = $(6.83 \pm 1.19) \times 10^{-12} \exp(-646 \pm 47/T)$ cm^3 molecule^{-1} s^{-1}.

The present results are compared to previous investigations and are theoretically discussed. The implications of these results on modeling of terrestrial and planetary atmospheres and also in combustion chemistry are discussed.

INTRODUCTION

The reaction between hydroxyl radicals and acetylene is important in terrestrial[1] and planetary atmospheric chemistry[2,3] as well as in combustion chemistry.[4,5] Thus, for example, the presence of CO in the reducing atmosphere of Jupiter has been explained with chemical models involving reactions of O and OH.[2,3] Which model contributes probably depends on a variety of atmospheric conditions. In the model of Prather, Logan and McElroy,[3] one of the principal paths to CO formation is the reaction sequence: $H_2O + h\nu \rightarrow H + OH$, $OH + C_2H_2 \rightarrow CH_2CO + H$, $CH_2CO + h\nu \rightarrow CH_2 + CO$. Both H_2O and C_2H_2 have been identified in the Jovian atmosphere, the latter being a product of CH_4 chemistry in the atmosphere of that planet.[6]

The role of the reaction

$$OH + C_2H_2 \rightarrow \text{products} \qquad (1)$$

in atmospheric and combustion chemistry has prompted several previous studies of both the products of the reaction and the absolute rate constant. Kanofsky et al.[7] showed in a crossed molecular beam-mass spectrometric experiment that C_2H_2O was a product. Thus, there is an open reactive pathway at room temperature and very low pressure. If this is the only pathway then it can be argued that pressure dependence for the thermal rate constant may not exist, and the reaction yields C_2H_2O (probably ketene) and H atoms exclusively under any condition of temperature and pressure. On the other hand, if pressure dependence is observed in the thermal rate constant, then adduct formation is definitely indicated, and the product of the reaction becomes, at least in part, the stabilized adduct radical. The ratio of reactive pathways then may be both pressure and temperature dependent. The implications for modeling applications is clear; that is, more than one product can be formed which depends on the conditions of the system whether that system be a flame, the terrestrial troposphere, a polluted air mass, or a planetary atmosphere.

Several of the early rate constant determinations were carried out in a low pressure (~ 1 torr) discharge flow apparatus,[8-10] and at least two studies[9,10] agreed on a room temperature value of $\sim 2 \times 10^{-13}$ cm^3 $molecule^{-1}$

s^{-1}. A flash photolysis-resonance absorption (FP-RA) study[11] at 10-20 torr gave a 298 K value of $\sim 9 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} which indicated the possibility of a pressure effect. This study was followed by a 298 K flash photolysis-resonance fluorescence (FP-RF) study[12] which gave $(1.65 \pm 0.15) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. No pressure dependence was observed, and therefore the low pressure discharge flow results were corroborated by this most sensitive, and presumably more accurate, technique. The rate behavior would have been settled had it not been for a later FP-RF study[13] which showed a strong pressure dependence and which disagreed with all previous investigations giving a 298 K value at 200-400 torr Ar of 6.8×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

The temperature dependence was examined in only two of these studies.[11,13] There is apparent agreement in the Arrhenius parameters determined in these studies. Such agreement is suprising and may be fortuitous considering the difference in total pressure (10-20 torr[11] and 200 torr[13] respectively) and the strong pressure dependence observed in the later study.[13]

A consideration of the abovementioned work suggests a clear motivation for the present investigation. Even though modern and accepted experimental techniques have been utilized, the rate behavior is not well characterized, and clearly such a characterization is important for all modeling applications where this reaction plays a role in a complex chemical scheme.

EXPERIMENTAL

Experiments for the present kinetic study were performed by the flash photolysis-resonance fluorescence (FP-RF) technique. The apparatus and specific procedures are similar to those reported previously;[14] however, we have replaced the reaction cell and vacuum housing assembly with newly constructed equipment designed to significantly lower scattered background light compared to the earlier cell. Details of this new equipment have been reported recently.[15]

Flash photolysis of water is the source of OH radicals for the reported experiments. An interference filter (Ditric Optics, Inc., centered at 157.5 nm with a skewed FWHM of -13 and +25 nm, maximum transmittance 28%) is employed to spectrally isolate the photoflash light as well as to decrease scattered light due to photoflash interference. Using this filter, the initial yield of OH from the photodecomposition of H_2O was 19% compared to that with a LiF window (λ > 105 nm). This factor reflects the spectrally integrated effects of wavelength dependent transmission, H_2O absorption, and photoflash intensity. A microwave discharge of water saturated Ar at 17 torr produces OH resonance radiation (λ = 306 nm). Before entering the cell, this radiation is slightly focused and collimated by a lens and collimator system. The fluorescent photons are collected and focused with a lens-collimator-interference filter (Ditric Optics, Inc., 310 nm, FWHM = 11 nm) optical system onto an EMR 541 N photomultiplier tube. A multichannel analyzer operating in the multiscaling mode records the fluorescent photons in repetitive flashes.

Experiments were carried out at five temperatures from 228-413 K over wide ranges of total pressure and substantial variations of $[C_2H_2]$. A range of flash energies was also used; however, due to the presence of the 157.5 nm interference filter in the photoflash optical path, the variation of flash intensity is somewhat limited compared to that used in most other studies from this laboratory. Corrections for the diffusional loss of OH from the observed reaction zone were determined by means of experiments performed without added C_2H_2. The observed pseudo-first-order OH radical decay plots were strictly linear under all conditions.

Acetylene (Matheson, 99.6%) used in this study was further purified for preparation of mixtures by bulb-to-bulb vacuum distillation at 125 K, with the middle fraction being retained. Mass spectral analysis showed the sample to be 99.9% pure. Argon (Matheson, 99.9995%) for mixture preparation and argon (Goddard grade, water pumped) for the resonance lamp were both used without further purification. Deionized water was used as received in the discharge lamp, but was bulb-to-bulb distilled with the middle fraction collected for mixture preparation.

RESULTS

All of the reported experiments were carried out under pseudo-first-order conditions with $[C_2H_2] >> [OH]$. The decay of OH radicals is then given by

$$\ln[OH] = -k_{observed}t + \ln[OH]_o \qquad (2)$$

The observed pseudo-first-order decay constant is represented by

$$k_{observed} = k_{bi}[C_2H_2] + k_d \qquad (3)$$

where k_{bi} is the bimolecular rate constant for reaction (1), and k_d is the first-order rate constant for OH radical diffusion from the reaction volume viewed by the detector. $k_{observed}$ and k_d are obtained by linear least squares methods from plots of the logarithm of accumulated counts against time, where accumulated counts are proportional to [OH]. Examples of characteristic results for the reaction at 257, 298, and 413 K are shown in Figure 1. Equation (3) was used to calculate values of k_{bi} from $k_{observed}$.

Rate data for the reaction of OH radicals with C_2H_2 at the various experimental conditions employed in this study are presented in Table I. These results indicate that, with the exception of the lowest temperature studied (228 K), k_{bi} depends on the total pressure. This pressure effect becomes more pronounced with increasing temperature. In fact the present results indicate a substantially greater pressure dependence than heretofore suggested in any earlier work. In such a situation the assignment of the high pressure limits at each temperature becomes somewhat arbitrary in view of an absolute uncertainty in k_{bi} of ~ ± 10% at each pressure. For these assignments we have constructed plots of k_{bi} against pressure on the assumption that a smooth variation connects the values at each pressure. Also, for a chemically activated adduct, the limits at higher temperatures will be reached at higher pressures. We conclude that the high pressure limits are effectively reached above 450, 300, 150, 75, and 0 torr for temperatures of 413, 362, 298, 257, and 228 K, respectively. The high pressure limits are reported in Table I, and the smoothed curve variations of k_{bi} against pressure are shown graphically in Figure 2.

A linear least squares analysis of the high pressure values gives $(k_{bi})_\infty$

= (6.83 ± 1.19) x 10^{-12} exp(-646 ± 47/T) cm^3 $molecule^{-1}$ s^{-1} for $228 \leq T \leq 413$ K where the indicated errors are at the one standard deviation level. The present limiting high pressure values along with the linear least squares line are shown in Figure 3 as an Arrhenius plot.

DISCUSSION

A comparison of the present results with earlier absolute values is difficult in view of the magnitude of the pressure dependence. There are three room temperature values for k_1 which have been obtained by the low pressure (∼ 1 torr) discharge flow technique. Wilson and Westenberg,[8] with ESR detection of [OH], report nk_1 = 1 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} where n is an undetermined stoichiometry factor. With a similar detection technique, Breen and Glass[9] obtained (1.9 ± 0.6) x 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. In this latter work n was experimentally determined. Pastrana and Carr[10] obtained (2.0 ± 0.6) x 10^{-13} cm^3 $molecule^{-1}$ s^{-1} with resonance absorption detection of [OH]. Their value, in part, resulted from the assumption of the same stoichiometric correction as earlier obtained by Breen and Glass. None of the present experiments given in Table I were carried out under these low pressure conditions. We attempted some experiments at pressures as low as 5 torr, and, even though these results were highly scattered, they could not be reconciled with a value of k_1 approaching 2 x 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. Inspection of the graphical representation of our results in Figure 2 shows that an extrapolation to this low a value is not likely, and a "reasonable" extrapolation would indicate a temperature independent zero pressure value for k_{bi} of 4 x 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. Thus, a clear discrepancy exists between the present work and all of the low pressure discharge flow results, and the reasons for this are not clear. We point out that stoichiometry corrections have been necessary because of the relatively insensitive [OH] detection methods previously used. In order to resolve this discrepancy, additional discharge flow experiments with higher [OH] sensitivity may be necessary.

There are three additional studies, two of which have specifically examined the pressure dependence at room temperature. Work done at the University of Maryland with the FP-RF technique[12] shows no pressure dependence, and k_1 = (1.65 ± 0.15) x 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. These workers also examined the possibility of secondary reactions (i.e., increasing flash energy) as a perturbing influence on OH profiles. With flash energies of 500 J they were able to increase the apparent decay constant by about a factor of three. In the present FP-RF study we were able, in initial experiments, to confirm this flash energy effect, decay constants increasing by a factor of two from 80-300 J. Thus, all experiments in Table I were obtained at flash energies substantially less than 80 J, and over moderate changes of flash energy, the decay constants were invariant within combined errors for a particular condition. The present results, which are obtained under similar conditions to this earlier FP-RF work,[12] clearly disagree both in absolute magnitude and the pressure dependence of k_{bi}. One explanation may be that He was used as a diluent gas whereas Ar was used in the present work. We accordingly carried out some experiments at 298 K with He as diluent and the results were $(5.63 \pm 0.21) \times 10^{-13}$ and $(5.08 \pm 0.88) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 35 and 20 torr, respectively. These results are still in gross disagreement, being the same as those in Ar (Table I). Therefore, even though the same technique (FP-RF) has been used a discrepancy remains between this earlier work and the present. On the other hand, a somewhat later FP-RF study by Perry et al.[13] saw a clear indication of pressure dependence. Their constants ranged from $(3.60 \pm 0.36) \times 10^{-13}$ to $(6.95 \pm 0.90) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} from 25.5 to 399.8 torr, respectively. The present values are 5×10^{-13} (interpolated) and $(7.8 \pm 0.7) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, so that the only disagreement that exists which is outside of combined experimental errors, is in the low pressure values and the steepness of the fall off. Perry et al. were able to accommodate the low values of the discharge flow experiments whereas we cannot. Lastly, the results of Smith and Zellner[11] were obtained by the flash photolysis-resonance absorption technique at 10-20 torr He or H_2/N_2O. They report a value of 8.5×10^{-13} cm^3 $molecule^{-1}$ s^{-1} which is ~ 50% higher than the present value over the same pressure range. These workers apparently saw no pressure dependence in k_{bi}.

The temperature dependence has been measured by both Smith and Zellner[11] and Perry et al.[13] who report $k_{bi} = 1.99 \times 10^{-12} \exp(-253/T)$ and $k_{bi} = 1.91 \times 10^{-12} \exp(-312 \pm 201/T)$ cm^3 $molecule^{-1}$ s^{-1} respectively. Though these results would appear to be in agreement with one another, they are not since Smith and Zellner's work was carried out at relatively low pressure (10-20 torr) whereas the expression given by Perry et al. was based on results obtained at 200 torr Ar. Both Arrhenius expressions are shown in Figure 3 for comparison purposes with that obtained here, and a clear discrepancy exists with regard to Arrhenius parameters between both earlier studies and the present work. We do note that the rate constants reported in the study by Perry et al. agree well with the present work. Our values at 200 torr Ar (Figure 2) are 7.7×10^{-13}, 8.7×10^{-13} and 10.9×10^{-13} cm^3 $molecule^{-1}$ s^{-1} (errors, ± 10%) at 298, 362, and 413 K, respectively. Perry et al. report $(6.79 \pm 0.70) \times 10^{-13}$, $(7.63 \pm 1.00) \times 10^{-13}$, and $(9.26 \pm 1.20) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298.1, 350.2, and 433.4 K, respectively. Thus, within combined experimental errors the results are identical. We, however, suggest that their derived Arrhenius parameters are not representative of the limiting values because they only reached the high pressure limiting rate constant at one temperature, 298 K.

The observation of pressure dependence as shown in Figure 2 clearly indicates the importance of a chemically activated adduct. Thermochemical arguments[16] ($C_2H_4 = C_2H_3 + H$, $OH + C_2H_3 = HOCHCH_2$, and $HOCHCH_2 = HOCHCH + H$) give $\Delta H^o_{f\ HOCHCH} = 28$ kcal/mole if the O-C bond energy in $HOCHCH_2$ is the same as in isoelectronic carboxylic acids, i.e., 107 kcal/mole. Then the exothermicity for adduct formation from $OH + C_2H_2$ is 36 kcal/mole with a probable uncertainty of at least ± 6 kcal/mole. Since the observed activation energy is 1.3 kcal/mole, the excess vibrational energy in the adduct is taken to be ~ 37 kcal/mole. These energy relationships are shown schematically in Figure 4.

The detailed mechanism then becomes:

$$OH + C_2H_2 \rightarrow HOCHCH^* \qquad k_1 \qquad (1)$$

$$HOCHCH^* \rightarrow OH + C_2H_2 \qquad k_\epsilon \qquad (4)$$

$$HOCHCH^* + M \rightarrow HOCHCH + M \qquad \omega \qquad (5)$$

However, this mechanism is incomplete since there is a finite rate constant at zero pressure. In fact, Kanofsky et al.[7] showed, in a crossed molecular beam-mass spectrometric experiment, that the low pressure product is C_2H_2O (and C_2DHO in the OH + C_2D_2 case), the overall process being:

$$OH + C_2H_2 = C_2H_2O + H. \qquad (6)$$

The product H atom is released from the acetylene molecule.

From a theoretical point of view there are two important questions: (1) what is the chemical identity of C_2H_2O, and (2) is process (6) an elementary reaction? These are also important practical questions for combustion, and for terrestrial and planetary atmospheric modeling.

With regard to the chemical identity of C_2H_2O, if it is hydroxyacetylene, HO-C ≡ CH, then process (6) is probably endothermic because breaking the acetylenic C-H bond requires ∼ 120 kcal/mole, and it is unlikely that the newly formed C-O bond will release this quantity. This situation is supported by recent quantum mechanical calculations[17] for hydroxyacetylene which indicate that this molecule is 36 kcal/mole less stable than ketene. Thus, process (6) would be endothermic by ∼ 10 kcal/mole. On the other hand, if C_2H_2O is ketene, CH_2CO, then process (6) is exothermic by 26 kcal/mole. Thus, ketene formation would be preferred on energetic grounds. The energy relationships are also shown schematically in Figure 4.

Concerning the question of process (6) being an elementary reaction, such a proposition would require that OH react with acetylene in two entirely different ways, one to form vibrationally excited adduct and the other to form C_2H_2O and H in a concerted process. Then the present results can be interpreted as the pressure dependent process simply adding on to the pressure independent concerted reaction, process (6), which has a temperature independent rate constant of ∼ 4×10^{-13} cm^3 $molecule^{-1}$ s^{-1}. This view then suggests a value of $(1.6 \pm 0.4) \times 10^{-11} \exp(-1134 \pm 64/T)$ cm^3 $molecule^{-1}$ s^{-1} for the high pressure limiting rate constant for the adduct pathway. Though we concede that this scheme is possible, an empirical comparison with OH plus unsaturated hydrocarbon reactions[1,18] indicates that an A factor in excess of 10^{-11} cm^3 $molecule^{-1}$ s^{-1} and an activation energy of 2.3 kcal/mole are both probably too large. Because of this, a second possibility exists; namely that process (6) is not an elementary reaction, and the low pressure products arise from the chemically activated species.

The detailed mechanism then consists of reactions (1), (4), (5) and,

$$HOCHCH^{*} \rightarrow OCHCH_2^{*} \qquad k_\epsilon' \qquad (7)$$

$$OCHCH_2^{*} \rightarrow CH_2CO + H. \qquad k_\epsilon'' \qquad (8)$$

Our view is that $k_\epsilon'' \gg k_\epsilon'$ so that ketene formation is determined by the rate of the isomerization reaction (7). This reaction suggests the formation of a strained activated complex but is probably thermoneutral. The energy relationships for these species are also given in Figure 4.

The mechanism, reactions (1), (4), (5), (7) and (8), with the steady state assumption for the vibrationally excited adducts, yields:

$$\frac{k_{bi}}{k_1} = \int_{\epsilon_0}^{\infty} \frac{(k_\epsilon' + \omega)\, f(\epsilon)\, d\epsilon}{(k_\epsilon + k_\epsilon' + \omega)} = D' + S, \qquad (9)$$

where $f(\epsilon)$ is the normalized distribution function for the formation of initially excited adduct radicals, and both k_ϵ and k_ϵ' are energy dependent. Equation (9) predicts that at zero pressure ($\omega = 0$) there will be a finite rate constant, $k_{bi} = k_1 \langle k_\epsilon' / (k_\epsilon + k_\epsilon') \rangle$, whereas at infinite pressure ($\omega \rightarrow \infty$), $k_{bi} = k_1$.

Since equation (9) predicts that $(k_{bi})_\infty = k_1$, the present high pressure results can be interpreted as the rate constant for the addition process; i.e., $k_1 = (6.83 \pm 1.19) \times 10^{-12} \exp(-646 \pm 47/T)$ cm^3 $molecule^{-1}$ s^{-1}. We note that A factors for OH with olefin reactions, which presumably also occur through adduct formation, have similar values.[1,18] The present A factor can also be discussed in terms of activated complex theory. With known partition functions, $A = (7.6 \times 10^{-31}/T)\, R_R\, q_v^{\dagger}$ (molecular units), where R_R is the moment of inertia ratio $[(I_1 I_2 I_3)^\dagger]^{1/2}/I_{OH}I_{CH}$ and $q_v^\dagger$ is the vibrational partition function for the activated complex (q_{vOH} and q_{vCH} are both unity over the present range of temperature). Calculations for the principal moments of inertia of the activated complex have been performed for C_s symmetric complexes at various C-O bond distances. These parametric calculations with the present A factor imply values for $q_v^\dagger$. We find that for a C-O distance of 2 Å, the present A factor is implied if two degenerate bending vibrations of 250 cm^{-1} contribute to $q_v^\dagger$ in the activated complex. A bending vibration of 250 cm^{-1} can be justified from structural considerations, bending vibrations of fully bonded similar molecules, and empirical correlations given by Johnston.[19] Thus, the model is reasonable.

Any quantitative attempt to evaluate equation (9) in order to predict the pressure fall off curves requires an accurate knowledge of the thermochemistry. Since such accuracy is not available nor can it be guessed with confidence, we have elected not to define the other activated complexes and carry out a full RRKM calculation. Instead we have simply shown in Figure 5 with RRK theory, how the present data can be qualitatively rationalized. In this figure, equation (9) is evaluated with assumptions for n, k_ϵ, k_ϵ', ϵ_0 and ϵ_0'. We presume that the frequency factor for the four center isomerization reaction (7) is much less than that for simple bond fission in reaction (4). We also assume that the strain energy involved in the isomerization reaction (7) is $\sim$ 28 kcal/mole.[16]

Figure 5 also indicates the fractions which yield decomposition products, D' and stabilized radicals, S, as functions of pressure, where D' and S are respectively, $\langle k_\epsilon'/(k_\epsilon + k_\epsilon' + \omega) \rangle$ and $\langle \omega/(k_\epsilon + k_\epsilon' + \omega) \rangle$. This qualitative illustration suggests the strong possibility that decomposition is rapidly pressure quenched in favor of stabilization. Therefore, the major product of the reaction in most atmospheric systems is the HOCHCH radical. The same may be true in high pressure combustion systems; however, in this case other competing reaction channels may be opened. For example (see Figure 4) the reaction through the endothermic pathway, HO-C $\equiv$ CH + H, may become important. This route might also arise from initially excited adduct,

$$\mathrm{HOCHCH}^* \rightarrow \mathrm{HOCCH} + \mathrm{H} \qquad k_\epsilon''' \tag{10}$$

However, k''' would be higher lying (10 kcal/mole according to Tanaka and Yoshimine[17]) than k_ε in Figure 5 in view of the aforementioned energy relationships. Because of these relationships and the observation of no pressure dependence at low temperature (a strong pressure effect would be predicted at 228 K if reaction (10) and not (7) were important), this pathway can be considered to be negligible over the present temperature range. However, at higher temperatures (broader activation function, $f(\varepsilon)$) this reaction channel might open thereby yielding HO-C ≡ CH and H as products. If this channel opens, hydroxyacetylene rearrangement to ketene may only occur slowly since the activation barrier has also been estimated in the previously cited quantum mechanical calculations[17] to be 73 kcal/mole.

CONCLUSIONS

The reaction between OH and C_2H_2 is not simple. The study by Kanofsky et al.[7] to characterize the products at low pressure, though elegant in its approach, may have little relationship with what occurs in complex practical systems where this reaction plays a role. In terrestrial and planetary atmospheric environments where the pressure is $\sim$ 1 atm, the most probable product of the reaction is the pressure stabilized HOCHCH radical, and the rate constant for the reaction is $(k_{bi})_\infty = k_1 = (6.83 \pm 1.19) \times 10^{-12} \exp(-646 \pm 47/T)$ cm^3 $molecule^{-1}$ s^{-1}. We thereby question the explanation for CO production on Jupiter recently given by Prather et al.,[3] particularly at lower more dense altitudes.

We further suggest that since product distributions are pressure and temperature dependent, a careful consideration of environmental conditions is necessary for data analysis and for modeling purposes. This point can be nicely illustrated in the combustion application. The high temperature reaction of OH with C_2H_2 has long been considered to be metathetical producing $C_2H + H_2O$.[20] This view is supported in two recent modeling reports,[5b,21] and this abstraction reaction is the only process considered in Westley's review.[4] The modeled data were mostly obtained in high pressure systems, and two abstraction rate constants are recommended, $k_{abs} = 1.3 \times 10^{-11} \exp(-2335/T)$[4] or $1.0 \times 10^{-12} \exp(-3523/T)$[5b] cm^3 $molecule^{-1}$ s^{-1}. We note that the present addition rate constant is always higher, up to even 2500 K, than either of these which are recommended for the abstraction path. Clearly, adduct formation and chemical activation should be considered in high pressure combustion systems. Such formation has been tacitly considered in other experimental[5a] and modeling[22] studies. Vandooren and Van Tiggelen[5a] have observed C_2H_2O in low pressure (40 torr) and low temperature (570-850 K) acetylene-oxygen flames. They derive a rate constant value for $OH + C_2H_2 = C_2H_2O+H$ of $5.3 \times 10^{-13} \exp(-100/T)$ cm^3 $molecule^{-1}$ s^{-1}. At 40t and $T \geq 570$ K, the reaction would undoubtedly be at or near the low pressure limiting value, and their value agrees very well with the low pressure, temperature independent value of 4×10^{-13} cm^3 $molecule^{-1}$ s^{-1} reported here. On the other hand, care must be taken to infer the same process exclusively in the modeling of high pressure flame and shock tube data because stabilization of the adduct radical may be a competitive process. Unfortunately the chemical mechanisms will then be more complicated than heretofore considered.

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TABLE I. Rate Data for the Flash Photolysis-Resonance Fluorescence Study of the Reaction OH + C_2H_2

(K)	$[C_2H_2]$ (mtorr)	$[H_2O]$ (mtorr)	[Ar] (torr)	Flash Energy[a] (J)	No. of expts.	k_{bi}[b] 10^{-13} cm^3 $molecule^{-1}$ s^{-1}
228	8.00	40	10	30-49	3	3.95 ± 0.39
	8.00	40	20	30-55	3	3.78 ± 0.28
	16.0	80	20	30-49	3	3.86 ± 0.12
	14.0	70	35	35-60	3	3.84 ± 0.25
	28.0	140	35	39,49	2	3.58 ± 0.26
	12.5	63	50	24-45	3	3.88 ± 0.03
	20.0	100	50	39,49	2	4.05 ± 0.13
	18.8	94	75	24-47	3	3.61 ± 0.17
	25.0	125	100	40-47	3	4.00 ± 0.36
	Average of expts. from 10-100 torr				25	3.84 ± 0.25
257	6.25	31	10	11-47	3	4.77 ± 0.29
	16.0	60	10	26-49	3	4.22 ± 0.39
	12.0	60	15	18-49	3	5.11 ± 0.33
	24.0	90	15	18-49	3	4.46 ± 0.36
	12.5	63	20	31-52	3	5.36 ± 0.49
	16.0	80	20	18-49	3	4.79 ± 0.11
	32.0	120	20	26-49	3	4.69 ± 0.34
	20.0	100	25	18-52	3	4.71 ± 0.69
	10.9	55	35	24,35	2	5.64 ± 0.34
	21.9	109	35	27-52	3	5.49 ± 0.31
	15.6	78	50	18-57	6	5.20 ± 0.27
	7.51	47	75	31-57	3	5.82 ± 0.75
	23.5	117	75	15-52	6	5.74 ± 0.36
	10.0	63	100	31,43	2	6.09 ± 0.76
	15.0	94	150	24-52	3	6.32 ± 0.43
	20.0	125	200	27-52	3	6.16 ± 0.43
					52	
	Average of expts. from 75-200 torr				17	5.97 ± 0.50[c]
298	6.26	31	10	30-55	3	4.95 ± 0.32
	8.00	80	10	20-49	3	5.09 ± 0.14
	5.50	18	20	26-55	3	5.07 ± 0.20
	8.00	40	20	31-43	3	5.04 ± 0.33
	8.00	80	20	24-51	3	5.35 ± 1.00
	12.5	63	20	26-55	3	5.42 ± 0.04
	16.0	160	20	20-49	3	5.00 ± 0.63
	9.63	31	35	26-55	3	5.60 ± 0.71
	14.0	70	35	27-43	3	5.38 ± 0.32
	14.0	140	35	36,48	2	5.39 ± 0.64
	21.9	109	35	6-55	5	5.90 ± 0.45

	28.0	280	35	36,49	2	6.23 ± 0.30
	5.06	33	50	30,55	2	6.22 ± 0.08
	13.8	44	50	26–55	3	6.34 ± 0.30
	15.6	78	50	30–55	3	5.90 ± 0.34
	20.0	100	50	27–43	4	5.52 ± 0.37
	20.0	200	50	36,51	2	6.17 ± 0.35
	7.59	49	75	30,55	2	7.86 ± 0.78
	20.6	66	75	26–55	3	6.85 ± 0.21
	23.5	117	75	30–55	3	6.83 ± 0.71
	10.1	65	100	30,55	2	7.79 ± 0.32
	13.8	44	100	30–55	3	6.65 ± 0.29
	20.0	100	100	11–36	3	6.70 ± 0.62
	20.0	200	100	37,49	2	6.54 ± 0.70
	15.2	98	150	42,55	2	8.76 ± 0.29
	20.6	66	150	30–55	3	8.04 ± 1.02
	5.61	40	200	45,55	2	8.11 ± 0.04
	20.3	130	200	30–55	3	8.03 ± 0.35
	40.0	200	200	36	2	6.46 ± 0.74
	6.10	44	300	47,55	2	6.96 ± 0.18
	8.42	60	300	45,55	2	7.95 ± 0.93
	8.13	59	400	45,55	2	7.46 ± 0.08
	11.2	80	400	49,55	2	8.18 ± 0.13
	12.2	88	600	47,55	2	7.75 ± 0.06
	16.8	120	600	52,55	2	7.45 ± 0.27
					92	
Average of expts. from 150–600 torr					24	7.76 ± 0.73^{c}
362	12.5	40	10	26–49	3	6.09 ± 0.50
	6.00	40	20	26–49	3	4.70 ± 0.15
	12.5	60	20	26–49	3	5.60 ± 0.38
	25.0	80	20	26–49	3	4.32 ± 0.43
	9.00	60	30	26–49	3	5.14 ± 0.59
	18.8	90	30	26–49	3	5.24 ± 0.41
	12.0	80	40	26–49	3	5.28 ± 0.42
	25.0	120	40	26–49	3	5.75 ± 0.52
	12.5	63	50	35,49	2	4.86 ± 0.81
	31.3	150	50	35,49	2	6.12 ± 0.19
	18.8	94	75	35,49	2	5.13 ± 0.75
	12.1	60	100	35–60	4	6.85 ± 0.53
	12.7	63	100	35–49	3	6.29 ± 1.08
	18.0	91	100	35,49	2	7.48 ± 0.12
	24.2	120	100	35–60	4	6.24 ± 0.56
	25.0	125	100	35,49	2	5.90 ± 0.06
	14.0	68	150	35–60	3	7.13 ± 0.61
	18.2	90	150	35–60	4	7.96 ± 0.27
	19.0	94	150	49	2	6.92 ± 0.23
	27.0	137	150	35–60	3	8.16 ± 0.15
	9.00	49	200	35–55	3	8.99 ± 0.61
	18.7	90	200	35–60	3	7.03 ± 1.20
	24.3	120	200	49–60	3	7.23 ± 0.63
	25.3	125	200	35–49	4	7.76 ± 0.75
	7.06	56	300	45,55	2	9.85 ± 0.11

	9.00	48	300	55	1	11.08
	13.5	74	300	35-55	3	9.73 ± 0.59
	24.2	120	300	45-60	3	8.11 ± 0.82
	9.41	75	400	45-55	3	11.32 ± 0.93
	12.0	64	400	60	1	13.87
	18.0	90	400	55	1	10.70
	18.0	99	400	35-58	3	10.57 ± 0.93
	14.1	112	600	55	3	11.81 ± 1.22
	18.0	96	600	60	1	11.72
					91	
Average of expts. from 300-600 torr					21	10.56 ± 1.56[c]
413	15.6	78	25	24-52	4	4.84 ± 0.40
	8.41	44	35	21-52	3	5.24 ± 1.03
	21.9	109	35	27-57	4	5.71 ± 0.33
	12.0	63	50	24-47	4	7.27 ± 0.33
	15.6	78	50	27-52	4	5.27 ± 0.67
	23.4	117	75	27-52	4	6.70 ± 0.45
	12.5	156	100	31-52	3	7.08 ± 0.54
	31.3	156	100	27-52	4	7.98 ± 0.27
	18.8	234	150	27-52	3	9.58 ± 0.72
	16.7	200	200	24-52	4	11.52 ± 1.02
	25.1	313	200	27-52	3	10.41 ± 0.05
	8.80	120	300	24-57	4	10.73 ± 1.13
	25.0	300	300	24-47	3	12.09 ± 0.73
	13.2	180	450	21-57	4	13.16 ± 0.92
	18.8	225	450	25-43	3	15.37 ± 1.05
	17.6	240	600	21-47	4	15.85 ± 1.61
	25.0	300	600	35-52	3	15.13 ± 0.89
	11.8	203	800	52	1	17.92
	16.2	279	1100	52	1	14.38
					63	
Average of expts. from 450-1100 torr					16	14.99 ± 1.63[c]

a. Effective flash energy through 157.5 nm filter.
b. Uncertainty in k_{bi} is one standard deviation.
c. Limiting high pressure rate constant.

FIGURE CAPTIONS

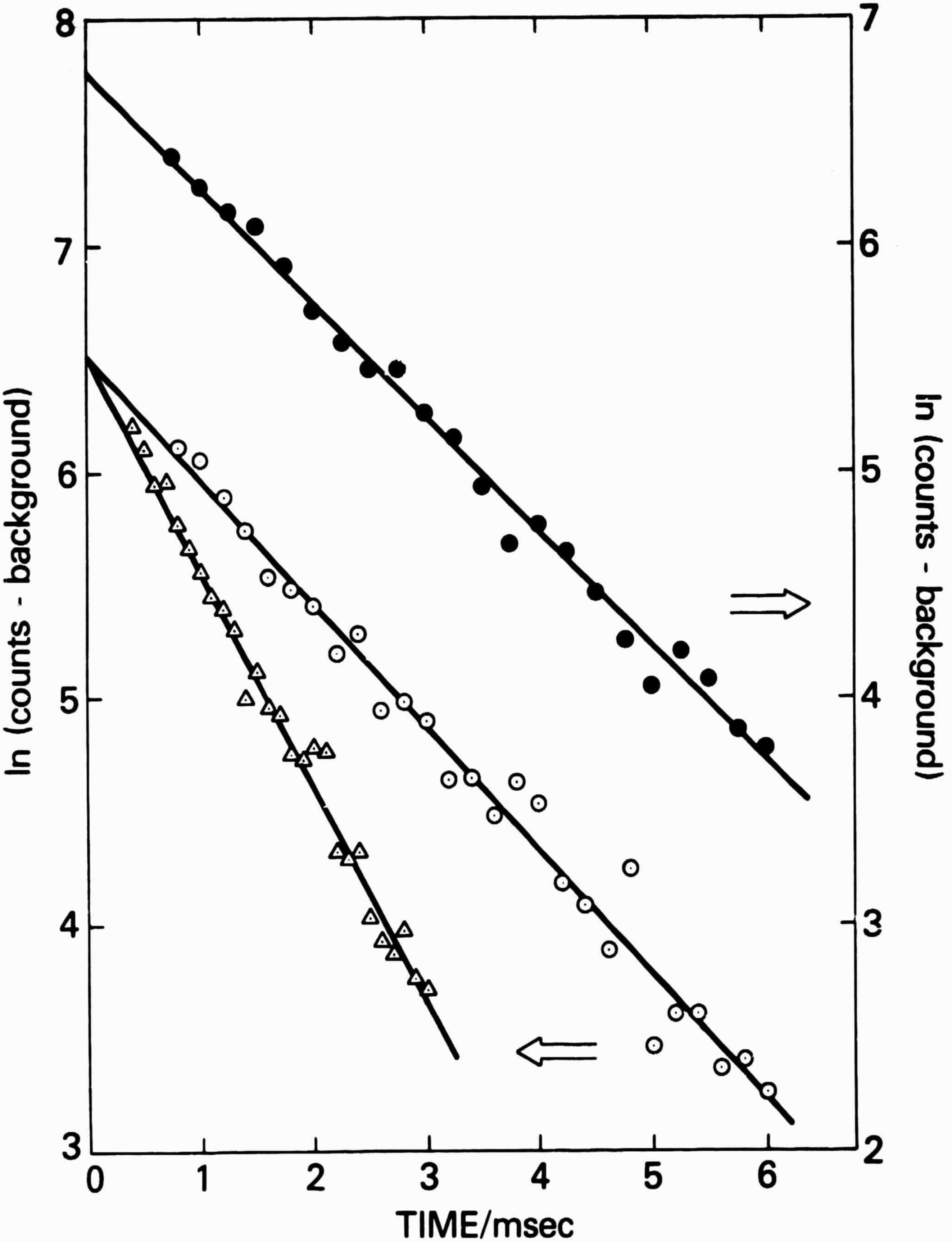
Fig. 1. Typical decay constants of the logarithm of OH fluorescent counts minus background against time. ●-T = 257 K, P_T = 200 torr, $P_{C_2H_2}$ = 20.0 mtorr, P_{H_2O} = 125 mtorr, $k_{observed}$ = 505 ± 13 s^{-1}; O-T = 298 K, P_T = 200 torr, $P_{C_2H_2}$ = 20.3 mtorr, P_{H_2O} = 130 mtorr, $k_{observed}$ = 545 ± 16 s^{-1}; Δ-T = 413 K, P_T = 600 torr, $P_{C_2H_2}$ = 25.0 mtorr, P_{H_2O} = 300 mtorr, $k_{observed}$ = 961 ± 23 s^{-1}.

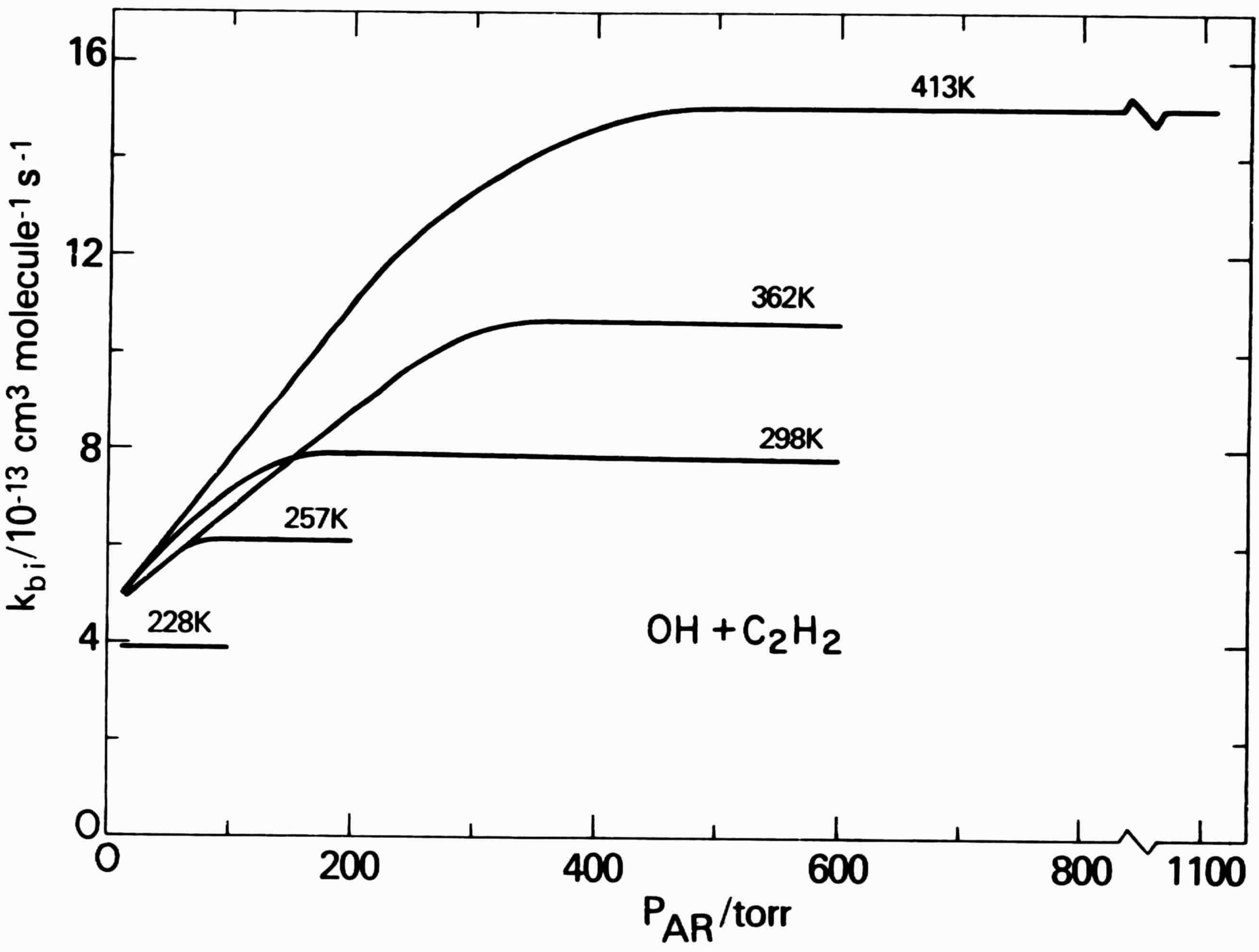
Fig. 2. Smoothed plot of the data in Table I at the five experimental temperatures. The estimated error in k_{bi} is $\sim$ ±10% at any pressure and/or temperature.

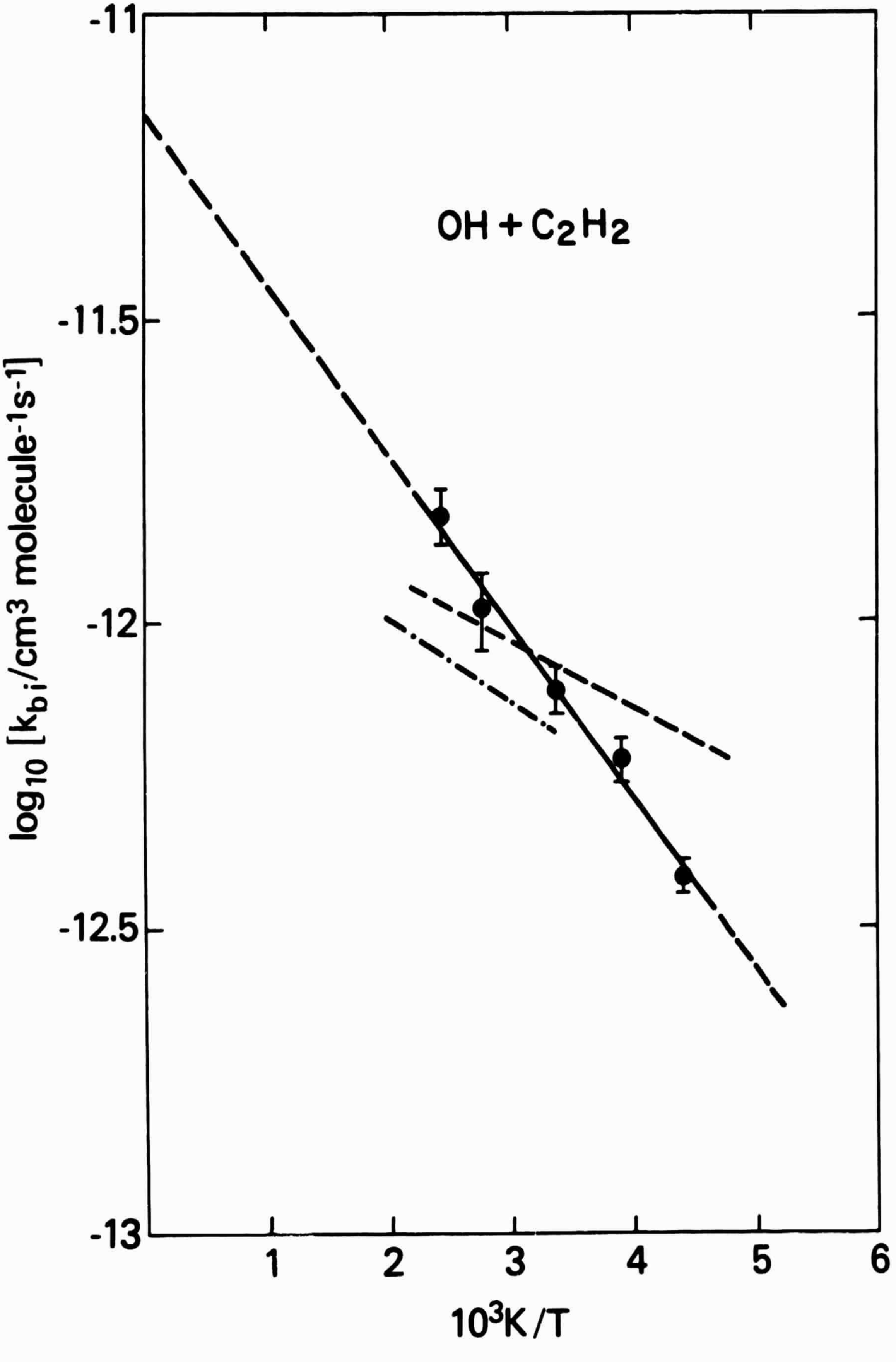
Fig. 3. Arrhenius plot of the high pressure bimolecular rate constant. ●-present data with one standard deviation error limits; the linear least squares line is given by $(6.83 \pm 1.19) \times 10^{-12} \exp(-646 \pm 47/T)$ cm^3 $molecule^{-1}$ s^{-1}. ---- results of Smith and Zellner.[11] _._._ results of Perry, Atkinson, and Pitts.[13]

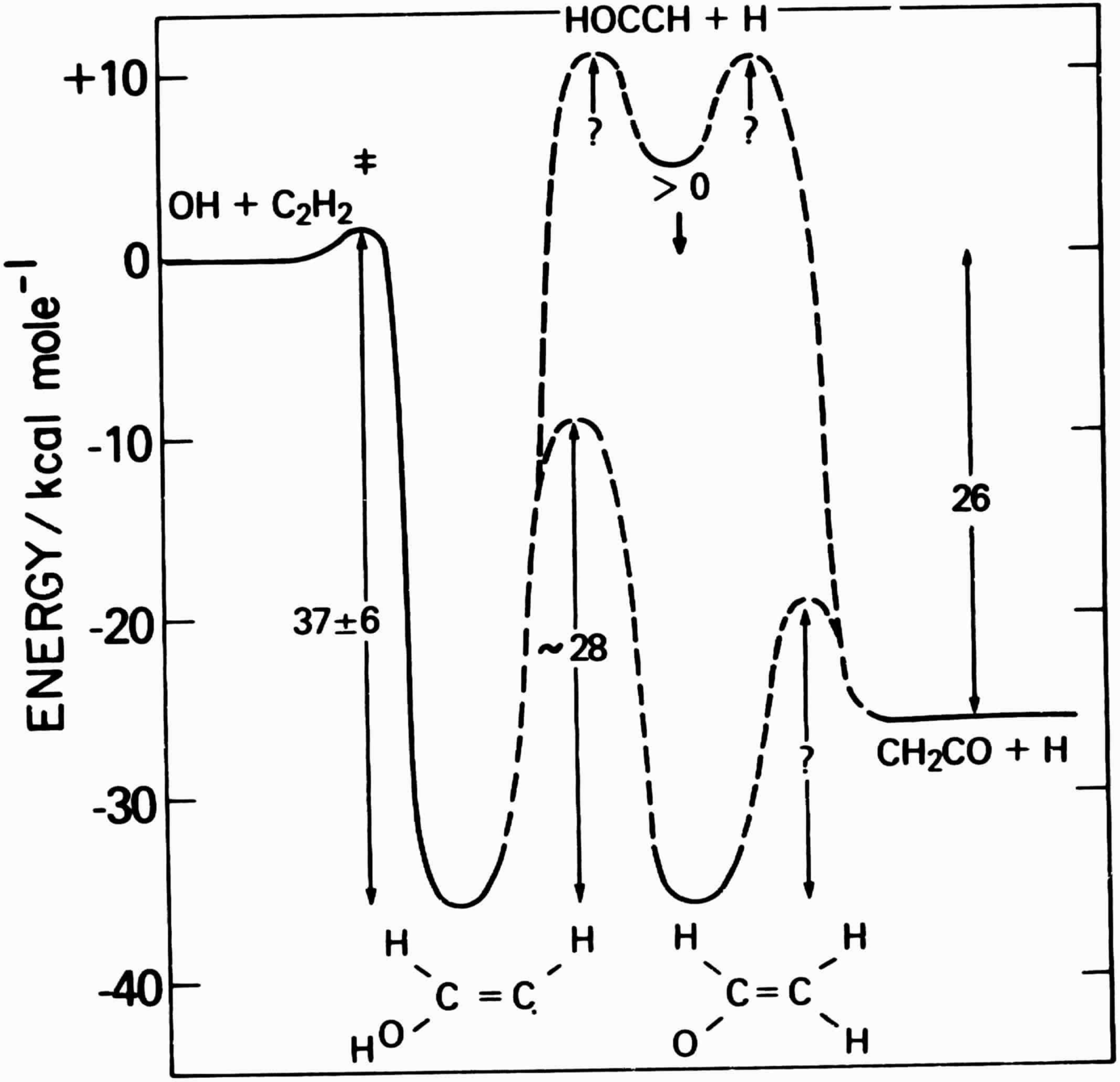
Fig. 4. Estimated energy relationships for the species which are presumed to be formed in the adduct pathway for the OH + C_2H_2 reaction (see text).

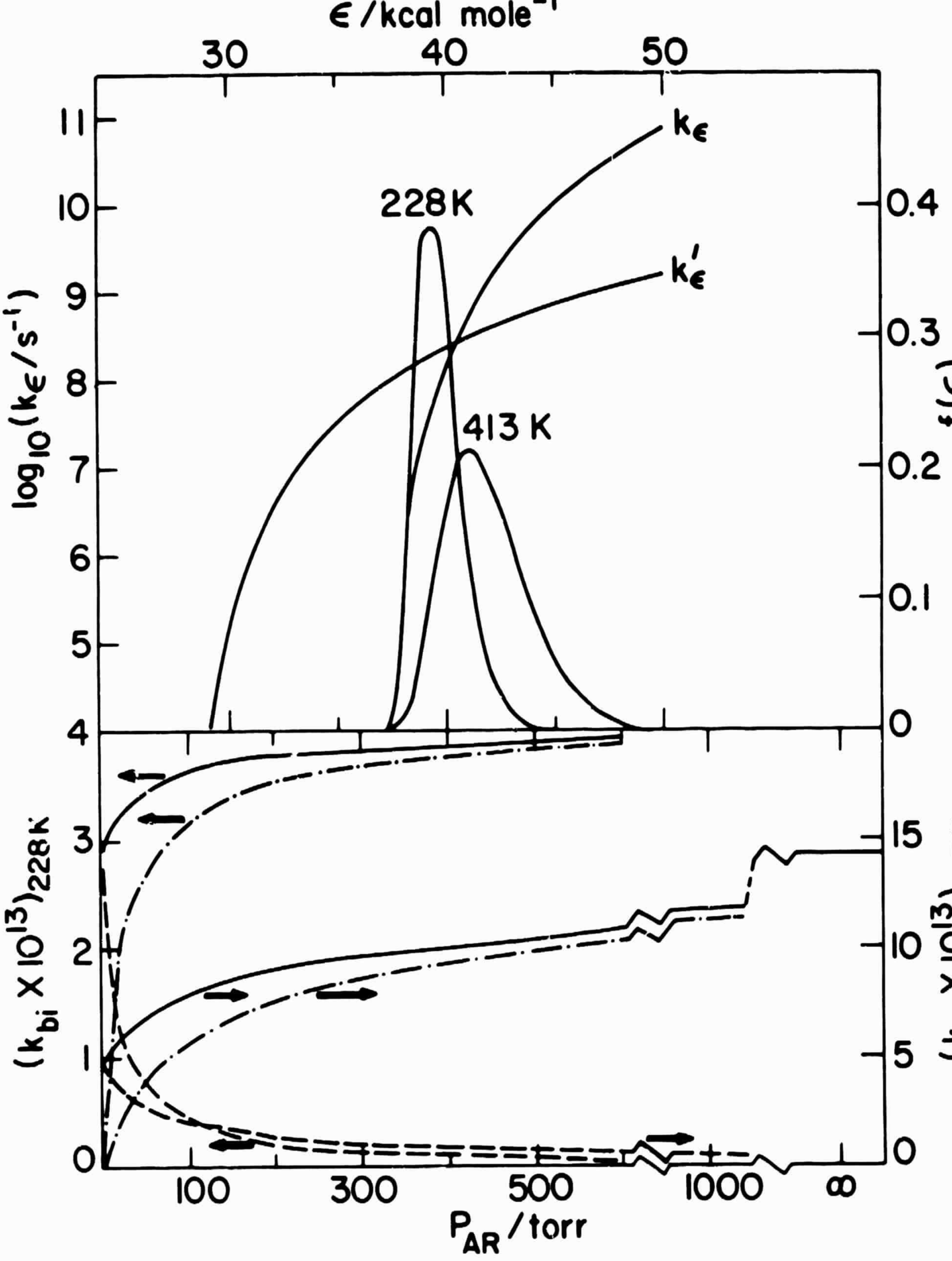
Fig. 5. Qualitative RRK calculation showing how behavior similar to that observed for OH + C_2H_2 can be rationalized. Calculations are for 228 K and 413 K. Upper frame shows $f(\varepsilon)$, k_ε, and k_ε'. $f(\varepsilon) = k_\varepsilon K(\varepsilon)\, d\varepsilon / \int_{\varepsilon o}^{\infty} k\varepsilon K(\varepsilon)\, d\varepsilon$ where $K(\varepsilon) = [\varepsilon^{n-1}/(kT)^n (n-1)!] \exp(-\varepsilon/kT)$, $n = 6$, $k_\varepsilon = 6\text{x}10^{13}$ s^{-1} $(\varepsilon-\varepsilon_o/\varepsilon)^{n-1}$, $k_\varepsilon' = 1\text{x}10^{11}$ s^{-1} $(\varepsilon-\varepsilon_o'/\varepsilon)^{n-1}$, ε_o = 37 kcal/mole^{-1}, ε_o' = 28 kcal mole^{-1}. Lower frame is an evaluation of equation (9) with $\omega = Z_{LJ}[M]$ where Z_{LJ} is the Lennard-Jones collision rate constant. Dashed line shows decomposition, D', and dot-dashed line shows stablization, S. Solid line is k_{bi} = D' + S (equation (9)).


8
7
6
5
4
3
7
6
5
4
3
2
ln (counts - background)
ln (counts - background)
0
1
2
3
4
5
6
TIME/msec


16
12
8
4
0
$k_{bi}/10^{-13}$ cm^3 molecule^{-1} s^{-1}
0
200
400
600
800
1100
P_{AR}/torr
413K
362K
298K
257K
228K
$OH + C_2H_2$


OH + C2H2
log10 [kb i/cm3 molecule-1s-1]
-11
-11.5
-12
-12.5
-13
1
2
3
4
5
6
10^3K/T


HOCCH + H
+10
0
-10
-20
-30
-40
ENERGY / kcal mole^{-1}
OH + C_2H_2
‡
?
?
> 0
37±6
~28
26
?
CH_2CO + H
H
C = C
HO
H
H
C = C
O
H
H



ϵ / kcal mole⁻¹
30
40
50
11
10
9
8
7
6
5
4
log₁₀(k_ϵ/s⁻¹)
0.4
0.3
0.2
0.1
0
f(ϵ)
k_ϵ
k′_ϵ
228K
413 K
4
3
2
1
0
(k_bi X 10¹³)₂₂₈K
15
10
5
0
(k_bi X 10¹³)₄₁₃K
100
300
500
1000
∞
P_AR / torr