

Kinetics of the Reactions of Unsaturated Hydrocarbon Free Radicals (Vinyl, Propargyl, and Allyl) with Molecular Bromine

R. S. Timonen,[†] J. A. Seetula,[†] and D. Gutman*

Department of Chemistry, Catholic University of America, Washington, D.C. 20064

Received: December 15, 1992; In Final Form: May 17, 1993

The kinetics of the reactions of three unsaturated free radicals (vinyl, propargyl, and allyl) with molecular bromine have been studied by using a tubular reactor coupled to a photoionization mass spectrometer. The radicals were homogeneously generated by the pulsed photolysis of precursor molecules at 193 nm. The subsequent decays of the radical concentrations were monitored in time-resolved experiments as a function of Br₂ concentration to obtain the rate constants of these Br-atom metathesis reactions. Rate constants were measured as a function of temperature to obtain Arrhenius parameters. The following rate constant expressions were obtained (units of the preexponential factor are cm³ molecule⁻¹ s⁻¹ and activation energies are kJ mol⁻¹; the temperature range covered in each study is also indicated): C₂H₃ + Br₂ {(4.0 ± 0.7) × 10⁻¹¹ exp((2.4 ± 1.5)/RT), 297–532 K}, C₃H₃ + Br₂ {(2.8 ± 0.5) × 10⁻¹² exp((-2.3 ± 1.2)/RT), 296–532 K}, and C₃H₅ + Br₂ {(4.8 ± 0.8) × 10⁻¹² exp((1.6 ± 0.8)/RT), 298–532 K}. The kinetics of R + Br₂ reactions is reviewed, and the factors governing the reactivity of polyatomic free radicals in R + Br₂ reactions are discussed.

Introduction

A picture of the reactivity of carbon-centered free radicals with molecular bromine is emerging from recent kinetic studies.^{1–5} The reactions of alkyl radicals with molecular bromine are quite exothermic ($\Delta H^\circ \approx -100$ kJ mol⁻¹) and generally have very high rate constants. Timonen et al.,³ who recently studied the kinetics of CH₃, C₂H₅, i-C₃H₇, and t-C₄H₉ with Br₂, reported reaction rate constants that are close to the respective collision numbers and which have small negative activation energies, indicating that the reactions proceed along attractive reaction paths. The reaction of HCO + Br₂ was found to display similar reactivity.² Halogen (Cl, Br, I) substitution on the radical center reduces reactivity. Timonen et al.,⁵ who also studied the kinetics of seven halogenated methyl radicals with Br₂, provided an explanation of this reduction using the inductive effect which was characterized using the sum of Pauling electronegativities of the substituent groups at the radical center.

As part of our ongoing investigation of the kinetics and thermochemistry of reactions of polyatomic free radicals with diatomic molecules containing halogen atoms, we have now studied the kinetics of three R + Br₂ reactions involving unsaturated free radicals, C₂H₃ (vinyl), C₃H₃ (propargyl), and C₃H₅ (allyl):



Two of these radicals (C₃H₃ and C₃H₅) have significant resonance stabilization energies (RSE), 46 kJ mol⁻¹ for C₃H₃^{6–8} (defined by the difference in bond enthalpies; RSE = DH(C₂H₅-H) - DH(propargyl-H)) and 51 kJ mol⁻¹ for C₃H₅^{9,10} (RSE = DH(C₂H₅-H) - DH(allyl-H)).¹¹

Little is known about the reactivity of C₃H₃ and C₃H₅ in atom-transfer reactions. Both radicals can readily be detected in pyrolysis and combustion processes,^{12–16} indicating a significant degree of stability not found in alkyl radicals. Timonen et al.¹⁷ investigated the kinetics of the reactions of C₂H₃, C₃H₃, and C₃H₅ with Cl₂. A major reduction of reactivity due to resonance stabilization was found among these R + Cl₂ reactions which

could be associated almost entirely with differences in reaction energy barriers (Arrhenius activation energies). There is no energy barrier in the C₂H₃ + Cl₂ reaction ($E_a = -2$ kJ mol⁻¹), but ones do exist in the C₃H₃ + Cl₂ (28 kJ mol⁻¹) and C₃H₅ + Cl₂ (18 kJ mol⁻¹) reactions. Loss of resonance stabilization in the R + Cl₂ reactions (i.e., in the formation of the RCl products) reduces exothermicity significantly, e.g., from about -136 kJ mol⁻¹ (C₂H₃ + Cl₂) to about -57 kJ mol⁻¹ (C₃H₃ and C₃H₅ + Cl₂), which probably accounts fully for the presence or absence of a reaction energy barrier.

In our current study, we have measured the rate constants of reactions 1–3 as a function of temperature both to extend our knowledge of the kinetics of free-radical reactions with molecular bromine and to determine the role of resonance stabilization on another set of atom-transfer reactions. Reaction 1, which involves an unsaturated radical of roughly comparable size to C₃H₃ and C₃H₅ and without resonance stabilization, acts as the reference reaction for this assessment.

Experimental Section

The experimental facility¹⁸ as well as its use for kinetic studies of reactions of polyatomic free radicals with Br₂ has been described.^{3–5} Only a summary will be presented here. Pulsed, unfocused, 193- or 248-nm radiation from a Lambda Physik EMG 201 MSC excimer laser was used to produce the radicals of interest. The laser beam was collimated and then directed along the axis of a heatable, 1.05-cm i.d. coated (with poly(tetrafluoroethylene)-Teflon 852-200 or Halocarbon Wax) tubular Pyrex reactor. Gas flowing through the tube (at ≈ 5 m s⁻¹) contained the free-radical precursor in very low concentration (typically 0.01–0.04%), Br₂ in varying amounts, and the carrier gas, He, in large excess (>99%).

Gas was sampled through a 0.4-mm diameter hole (located at the end of a nozzle in the wall of the reactor) and formed into a beam by a conical skimmer before it entered the vacuum chamber containing the photoionization mass spectrometer. Atomic resonance lamps are used to provide the ionizing radiation in the ion source of the mass spectrometer. As the gas beam traversed the ion source, a portion is photoionized and then mass selected.

Temporal ion-signal profiles were recorded from a short time before each laser pulse to as long as 26 ms following the pulse by using a multichannel scaler. Data from 2000 to 20 000

[†] Present address: Department of Physical Chemistry, University of Helsinki, SF-00170 Helsinki, Finland.

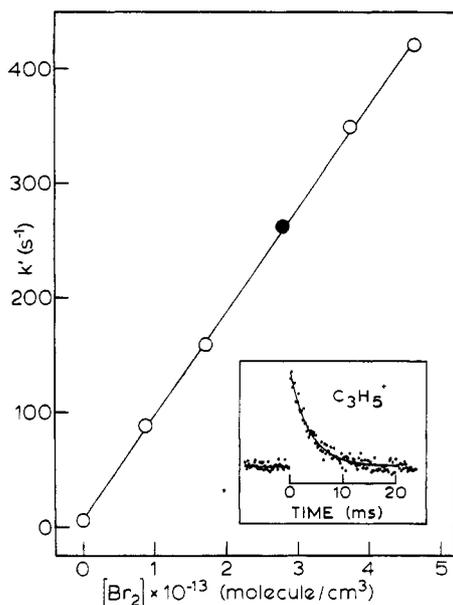
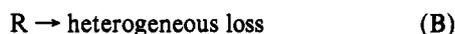


Figure 1. Plot of exponential decay constant of $C_3H_5^+$ ion signals (k') measured at 300 K. Insert is actual ion-signal profile of $C_3H_5^+$ recorded during one of the plotted experiments ($[Br_2] = 2.79 \times 10^{13}$ molecule cm^{-3}). The line through the data is an exponential function fitted by nonlinear least-squares procedures. The first-order decay constant (k') for $C_3H_5^+$ in the displayed ion signal profile is 262 ± 9 s^{-1} (filled circle).

repetitions of the experiment were accumulated before the data were analyzed.

Experiments were conducted under conditions where only two significant reactions consumed the labile reactant, R:



In all sets of experiments performed to determine a reaction rate constant, tests were also conducted to ensure that radical-radical and radical-atom reactions had negligible rates compared to either reaction A or B. Initial concentrations of R were reduced until the measured atom or radical decay constants in the presence or absence of the stable reactant no longer depended on the initial radical precursor concentration or on the laser fluence.

The laser fluence was attenuated by using quartz plates to reduce the photolysis of Br_2 to a negligible amount (<1%). The fact that the radical decay constants in the presence of Br_2 did not depend on laser fluence indicated that the limited amount of Br_2 photolysis that occurred did not interfere with the determinations of k_1 – k_3 . Laser fluences used were typically below 20 $mJ\ cm^{-2}$. Using the highly attenuated laser beam, the photolysis of the radical precursor was too low to measure. On the basis of previously measured radical sensitivities, the initial concentrations of the reactant radicals are estimated to be in the range $(1\text{--}8) \times 10^{10}$ radicals cm^{-3} .

In the experiments to measure k_1 – k_3 , Br_2 was always in great excess over the initial concentration of R. Rate constants for reactions 1–3 were obtained from slopes of plots of the radical exponential decay constant k' {from $[R]_t = [R]_0 \exp(-k't)$ } vs $[Br_2]$. A representative ion signal decay profile and a decay constant plot from one set of experiments to measure k_2 are shown in Figure 1.

In the case of one of the reactions studied, $C_3H_3 + Br_2$, two different wall coatings were used in the tubular reactor. No difference was found in the measured rate constants suggesting that heterogeneous effects were properly accounted for by reaction B (i.e., there were no bimolecular heterogeneous processes involving Br_2 occurring).

The bromides produced by reactions 1–3 could not be monitored, preventing confirmation of the products of the bromine

TABLE I: Conditions and Results of Experiments To Measure Rate Constants of the Reactions of C_2H_3 , C_3H_3 , and C_3H_5 with Molecular Bromine

T^a (K)	$[He] \times 10^{-16}$ (atom cm^{-3})	$[Br_2] \times 10^{-12}$ (molecule cm^{-3})	k_w (s^{-1})	wall coating material ^b	$k \times 10^{12}$ ($cm^3\ molecule^{-1}\ s^{-1}$)
$C_2H_3 + Br_2 \rightarrow C_2H_3Br + Br$ (k_1)					
297	4.80	1.41–4.16	97	PTFE	107
299	14.7	2.14–4.57	98	PTFE	103
358	4.69	2.19–5.09	99	PTFE	94.3
399	4.69	2.25–5.55	83	PTFE	80.2
456	4.72	2.81–6.19	98	PTFE	74.0
532	4.77	2.42–5.06	119	PTFE	70.0
$k_1 = (4.0 \pm 0.7)10^{-11} \exp[(2.4 \pm 1.5) \text{ kJ mol}^{-1}/RT]$					
$C_3H_3 + Br_2 \rightarrow C_3H_3Br + Br$ (k_2)					
296	4.79	65.4–199	12	PTFE	1.14
299	4.79	44.8–200	3.1	HW	1.17
358	4.68	36.3–198	4.2	HW	1.10
358	4.67	24.6–203	5.4	PTFE	1.26
399	4.70	57.7–201	4.1	PTFE	1.29
456	4.72	22.9–172	15	PTFE	1.44
532	4.78	26.1–119	31	PTFE	1.85
$k_2 = (2.8 \pm 0.5)10^{-12} \exp[(-2.3 \pm 1.2) \text{ kJ mol}^{-1}/RT]$					
$C_3H_5 + Br \rightarrow C_3H_5Br + Br$ (k_3)					
298	14.8	10.9–46.5	8.5	PTFE	9.30 ^c
300	4.98	8.87–46.4	6.1	PTFE	9.02 ^c
358	4.69	8.14–44.6	5.5	PTFE	8.11 ^c
399	4.70	9.15–45.0	2.8	PTFE	7.55 ^c
456	4.72	20.8–54.1	5.5	PTFE	7.28 ^c
532	4.79	12.7–52.6	9.9	PTFE	7.03 ^c
$k_3 = (4.8 \pm 0.8)10^{-12} \exp[(1.6 \pm 0.8) \text{ kJ mol}^{-1}/RT]$					

^a Temperature uncertainty: ± 2 K (296–358 K), ± 4 K (399–456 K), and ± 5 K (532 K). ^b Wall coating materials used: PTFE (poly(tetrafluoroethylene)) and HW (halocarbon wax). ^c Radical produced by 248-nm photolysis (photolysis at 193 nm used in all other experiments).

reactions. This is because these same bromides were used as the free-radical precursors, and their presence obscured detection of additional small amounts produced by the reaction under study.

The conditions of all experiments used to measure k_1 – k_3 and the results obtained are given in Table I. The rate constants obtained for these reactions are also displayed in an Arrhenius plot, Figure 2.

The reactants used were obtained from Matheson (vinyl bromide, 99.5%), Aldrich (allyl bromide, 99%; Br_2 , >99%), and TCI (propargyl bromide, >98%). The helium (99.995%) carrier gas was obtained from Matheson. The free-radical precursors and Br_2 were degassed using freeze–pump–thaw cycles. Helium was used as provided.

The photoionization energies used to detect reactants were 11.6–11.8 eV (argon lamp) to detect Br_2 , 10.2 eV (hydrogen lamp) to detect C_2H_3 , and 8.9–9.1 eV (chlorine lamp) to detect C_3H_5 and C_3H_3 .

Discussion

Comparisons with Prior Investigations. There has been only one prior investigation of any of the reactions studied. Slagle et al.¹ obtained a value of k_3 at 300 K, $9.0 (\pm 1.8) \times 10^{-11}$, using essentially the same experimental technique as was used in the current investigation. (Units used for bimolecular rate constants in this discussion are $cm^3\ molecule^{-1}\ s^{-1}$.) This value is in excellent agreement with the current determination at ambient temperature, 9.2×10^{-11} . The important difference between the prior and current study is the laser photolysis technique used. Both studies used C_3H_5Br as the radical source, but Slagle et al. used multiphoton infrared laser photolysis of the precursor molecule to produce the allyl radicals.

In studies such as the current one which use UV laser photolysis to produce free-radical reactants, there is always the question whether the internal energy of the radicals produced by photolysis

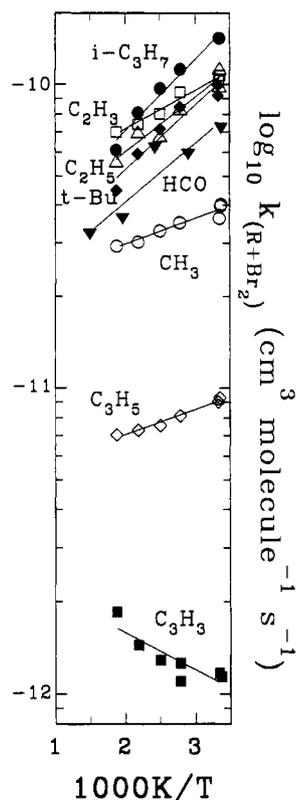


Figure 2. Arrhenius plot of measured $R + Br_2$ rate constants for reactions involving hydrocarbon radicals (plus HCO). Sources of rate constants given in Table II.

is thermalized before significant reaction takes place. Direct study of vibrational relaxation of polyatomic radicals^{19,20} as well as routine experiments in our laboratory (in which bath-gas density and/or bath gas identity is changed to alter vibrational relaxation times) indicates that thermal relaxation is fast compared to chemical reaction time under our experimental conditions. The fact that determinations of k_3 are the same if C_3H_5 is produced by decomposition of C_3H_5 from an excited electronic state (UV photolysis) or by decomposition from the ground electronic state (IR multiple-photon decomposition) further supports our conclusion that thermal relaxation is rapid (<0.2 ms) compared to chemical reaction time ($t_{1/2} = 2\text{--}50$ ms) over the range of conditions used in our experiments.

Summary of Reactivity in $R + Br_2$ Reactions. The kinetics of a total of 16 $R + Br_2$ reactions involving smaller carbon-centered free radicals have now been investigated in our laboratory. Reactivity varies widely as can be seen in the Arrhenius plot of these rate constants in Figures 2 and 3 and in the summary of reaction kinetics and thermochemistry given in Table II.

Major reactivity trends are very apparent in Figures 2 and 3. Rate constants of all hydrocarbon radicals with Br_2 (with the exception of the resonance stabilized radicals) are very high and comparable, approaching the respective collision numbers at ambient temperature.³ All display small negative activation energies (-2 to -4 kJ mol⁻¹). The HCO radical behaves similarly.²

Halogen substitution in the methyl radicals, as discussed before, reduces reactivity systematically.⁵ This reduction is manifested both in the Arrhenius A factors which decrease with increasing halogen substitution and the activation energies which increase as halogen atoms are added to the radical site. Timonen et al.⁵ provided a semiquantitative accounting for this reduced activity in terms of the inductive effect of all atoms attached to the carbon center, an effect which could be characterized by the sum of Pauling electronegativities of these atoms.

As expected, it was found that the resonance stabilized radicals, C_3H_3 and C_3H_5 , are much less reactive than is C_2H_3 , the reference

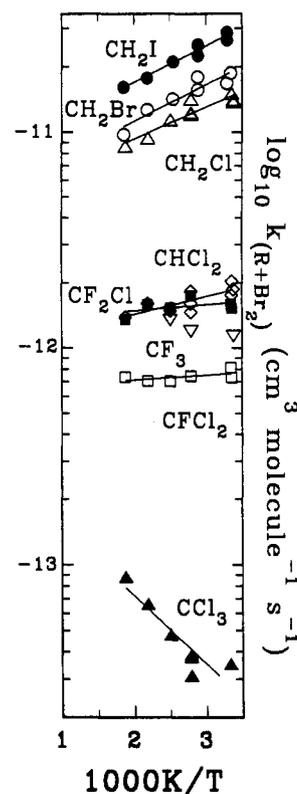


Figure 3. Arrhenius plot of measured $R + Br_2$ rate constants for reactions involving halogenated methyl radicals. Sources of rate constants given in Table II.

TABLE II: Summary of Arrhenius Rate Constant Parameters and Thermochemistry of the Reactions of Polyatomic Free Radicals with Molecular Bromine

radical	ΔH_f^a (kJ mol ⁻¹)	$\log_{10} A$ (cm ³ molecule ⁻¹ s ⁻¹)	E_a (kJ mol ⁻¹)	ref
<i>t</i> -C ₄ H ₉	-102	-10.71 ± 0.11	-4.1 ± 1.9	3
<i>i</i> -C ₃ H ₇	-105	-10.62 ± 0.11	-4.5 ± 1.9	3
C ₂ H ₅	-100	-10.58 ± 0.12	-3.4 ± 1.7	3
CH ₃	-103	-10.70 ± 0.08	-1.6 ± 1.1	3
CHO	-103	-10.78 ± 0.30	-3.7 ± 2.0	2
C ₂ H ₃	-121	-10.40 ± 0.08	-2.4 ± 1.5	cs ^b
C ₃ H ₅	-49	-11.32 ± 0.08	-1.6 ± 0.8	cs
C ₃ H ₃	-54	-11.56 ± 0.09	+2.3 ± 1.2	cs
CH ₂ I	-92	-11.11 ± 0.08	-3.2 ± 0.8	5
CH ₂ Br	-99	-11.29 ± 0.08	-3.2 ± 0.9	5
CH ₂ Cl	-83	-11.32 ± 0.08	-2.8 ± 0.8	5
CHCl ₂	-66	-12.01 ± 0.08	-1.6 ± 0.6	5
CF ₂ Cl	-78	-11.88 ± 0.09	-0.5 ± 1.3	5
CF ₃	-101	-11.69	+1.5	5
CFCl ₂	-60	-12.19 ± 0.08	-0.4 ± 0.8	5
CCl ₃	-32	-12.52 ± 0.08	+6.0 ± 1.2	5

^a Heats of formation used to determine reaction enthalpies were taken from the following sources: Br,²² Br₂,²² *t*-C₄H₉,²³ *i*-C₃H₇,²⁴ C₂H₅,¹¹ CH₃,²⁵ CHO,²² C₂H₃,²⁶ C₃H₅,⁹ C₃H₃,²⁷ CH₂I,²⁸ CH₂Br,²⁹ CH₂Cl,²⁹ CHCl₂,²⁹ CF₂Cl,³⁰ CF₃,²⁹ CFCl₂,²⁹ CCl₃,⁴ *t*-C₄H₉Br,²⁷ *i*-C₃H₇Br,²⁷ C₂H₅Br,²⁷ CH₃Br,²⁷ CHOBr,³¹ C₂H₃Br,²⁷ C₃H₅Br,²⁷ C₃H₃Br,²¹ CH₂IBr,³² CH₂Br₂,³³ CH₂ClBr,³⁴ CHCl₂Br,²⁷ CF₂ClBr,²⁷ CF₃Br,²⁷ CFCl₂Br,³² and CCl₃Br.³⁵
^b Current study.

unsaturated radical. Vinyl radical + Br_2 rate constants are comparable to those of the alkyl radical + Br_2 reactions indicating that unsaturation by itself does not reduce reactivity. Rate constants for the two $R + Br_2$ reactions that involve C_3H_3 and C_3H_5 are from 10–100 times below that of the $C_2H_3 + Br_2$ reaction at 298 K.

In the case of the reactions of these same three radicals with Cl_2 , the reduction of reactivity of the resonance stabilized radicals was easy to explain.¹⁷ It was due mostly to the higher activation energies of the $C_3H_3 + Cl_2$ and $C_3H_5 + Cl_2$ reactions (compared to the $C_2H_3 + Cl_2$ reference reaction), a fact which in turn could

be accounted for by the much lower exothermicity of the reactions involving the resonance stabilized radicals. Such a simple picture does not exist in the case of the corresponding $R + Br_2$ reactions. The $C_3H_5 + Br_2$ rate constants are about a factor of 10 lower than the $C_2H_3 + Br_2$ rate constants, due mostly to a lower Arrhenius A factor for the former reaction. The activation energies for the two reactions are very similar. On the other hand, the reduced reactivity of the $C_3H_3 + Br_2$ reaction is due to both a lower A factor and a higher activation energy than the $C_2H_3 + Br_2$ reaction (both factors contributing about equally to lowering the rate constant at 298 K).

Somewhat unexpected is the difference in reactivity between C_3H_3 and C_3H_5 in their reactions with Br_2 which appears counter indicated based on the thermochemical and physical properties of the radicals. Two properties of these radicals suggest that C_3H_5 should be the less reactive of the two, yet the opposite is the case. First, the C_3H_5 radical has the higher degree of resonance stabilization and hence is expected to be less reactive.⁶⁻¹⁰ Second, the electron affinity of the C_3H_5 radical (45.6 kJ mol^{-1})³⁶ is substantially less than that of C_3H_3 (86.2 kJ mol^{-1})³⁷ which also suggests that C_3H_5 should be the less reactive of the two resonance stabilized radicals. Alfasi and Benson³⁸ have demonstrated that, for the large group of atom-transfer reactions that they considered, $A + BC \rightarrow AB + C$, activation energies are reduced systematically as the end-group (A and C) electronegativities increase. The explanation offered for this effect is connected with the bonding in the reaction transition state, $A \cdots B \cdots C^\ddagger$, which is visualized as two one-electron bonds and one extra antibonding electron shared by A and C. From this standpoint, it was regarded as reasonable to assume that the activation energy will be less the higher the tendency of A and/or C to attract this extra electron. Equivalently, the higher the electron affinities of A and C, the lower the activation energy should be.

No explanation for the unexpected higher reactivity of C_3H_5 compared to that of C_3H_3 in these atom-transfer reactions is obvious. It is possible that the indicated reaction enthalpies of reactions 2 and 3 provide an incorrect picture of which of the two is more exothermic. The difference in reaction enthalpies is actually rather small, 5 kJ mol^{-1} . The combined probable errors in the heats of formation of C_3H_5 and C_3H_3 used to determine the two reaction enthalpies is most probably at least 5 kJ mol^{-1} .⁶⁻¹⁰ So it could be the case that reaction 3 is the more exothermic of the two reactions. If this is so, the observed difference in reactivity of C_3H_5 and C_3H_3 could be at least partially explained using the traditional thermochemical arguments. One indication that reaction 3 may actually be more exothermic than reaction 2 is the fact that the differences in the magnitudes of the rate constants for these two quite comparable reactions is associated almost entirely with the difference between the two reaction activation energies. Reaction 3 has a small negative activation energy (-1.6 kJ mol^{-1}) and reaction 2 a small positive one (2.3 kJ mol^{-1}). Both reactions are not very exothermic. It would appear based on these activation energies that reaction 3 is the more exothermic of the two reactions since reaction enthalpies can be expected to be influential in determining potential energy barriers here.

Comparison of $R + Br_2$ and $R + Cl_2$ Rate Constants. It is worth comparing the measured $R + Br_2$ rate constants with the corresponding $R + Cl_2$ rate constants since the thermochemistry of such pairs of reactions is quite similar, thus permitting observation of other factors which affect reactivity. (For example, ΔH° , for the $C_3H_5 + Br_2$ reaction is -49 kJ mol^{-1} , whereas that of the $C_3H_5 + Cl_2$ reaction is -55 kJ mol^{-1} .) For each R studied, the measured $R + Br_2$ rate constants are higher than those of the $R + Cl_2$ reaction. Differences are most dramatic if the $R + Cl_2$ reactions have a positive activation energy. This is the case for the C_3H_3 and $C_3H_5 + Br_2$ and Cl_2 reactions whose rate constants are plotted together in Figure 4. It is quite apparent that the higher reactivity of each of the two $R + Br_2$ reactions (compared

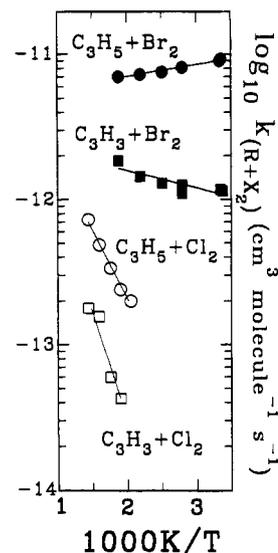


Figure 4. Arrhenius plot of the rate constants of C_3H_5 and C_3H_3 reactions with Br_2 and Cl_2 . $R + Br_2$ rate constants from current study. $R + Cl_2$ rate constants from ref 17.

with the corresponding $R + Cl_2$ reactions) is largely associated with its lower activation energy.

The explanation for the lower $R + Br_2$ activation energies must lie outside end-group electronegativity considerations and thermochemical factors which would predict activation energies for the $R + Br_2$ reactions that are actually higher than those of the $R + Cl_2$ reactions. The $R + Br_2$ reactions are slightly less exothermic than the $R + Cl_2$ reactions, and the electron affinity of Br (3.365 eV) is less than that of Cl (3.617 eV).²⁷

It has been clearly demonstrated by Krech and McFadden³⁹ that molecular polarizability of BC (e.g., Br_2 or Cl_2) stabilizes $A \cdots B \cdots C^\ddagger$ transition states (lowers activation energies). It is this property which is most probably responsible for the $R + Br_2$ activation energies being below those of the corresponding $R + Cl_2$ reactions.^{5,39} Br_2 has a considerably higher molecular polarizability ($69.9 \times 10^{-25} \text{ cm}^3$) than does Cl_2 ($46.1 \times 10^{-25} \text{ cm}^3$).⁴⁰

Summary

The kinetics of a large number of $R + Br_2$ reactions has now been investigated. Trends in rate constants have been noted and discussed. Resonance stabilization lowers reactivity significantly but not in an easily predictable manner.

Acknowledgment. We gratefully acknowledge support for this research from the National Science Foundation (CHE-9102038). We thank Dr. I. R. Slagle for her advice and assistance. J.A.S. thanks the Natural Science Council of the Academy of Finland for a fellowship. R.S.T. thanks the Maj and Tor Nessling Foundation for a fellowship. We thank Keith D. King (University of Adelaide), W. Tsang (NIST), and G. Barney Ellison (University of Colorado) for useful comments and information on C_3H_3 and C_3H_5 .

References and Notes

- (1) Slagle, I. R.; Yamada, F.; Gutman, D. *J. Am. Chem. Soc.* **1981**, *103*, 149.
- (2) Timonen, R. S.; Ratajczak, E.; Gutman, D. *J. Phys. Chem.* **1988**, *92*, 651.
- (3) Timonen, R. S.; Seetula, J. A.; Gutman, D. *J. Phys. Chem.* **1990**, *94*, 3005.
- (4) Hudgens, J. W.; Johnson, R. D. III; Timonen, R. S.; Seetula, J. A.; Gutman, D. *J. Phys. Chem.* **1991**, *95*, 4400.
- (5) Timonen, R. S.; Seetula, J. A.; Niiranen, J. T.; Gutman, D. *J. Phys. Chem.* **1991**, *95*, 4009.
- (6) Staker, W. S.; King, K. D.; Nguyen, T. T. *Int. J. Chem. Kinet.* **1992**, *24*, 781.
- (7) Tsang, W. *Int. J. Chem. Kinet.* **1970**, *2*, 23.

- (8) Tsang, W. *Int. J. Chem. Kinet.* **1978**, *10*, 687.
(9) Tsang, W.; Walker, J. A. *J. Phys. Chem.* **1992**, *96*, 8378.
(10) Tsang, W. *J. Phys. Chem.* **1986**, *90*, 1152.
(11) Based on $DH(C_2H_3-H) = 420.2 \text{ kJ mol}^{-1}$ from the C_2H_3 heat of formation: Brouard, M.; Lightfoot, P. D.; Pilling, M. J. *J. Phys. Chem.* **1986**, *90*, 445.
(12) Homann, K. H.; Wellman, Ch. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 609.
(13) Smith, R. D. *Combust. Flame* **1979**, *35*, 179.
(14) Bittner, J. D.; Howard, J. B. *Symp. (Int.) Combust. [Proc.] 19th* **1983**, 211.
(15) Westmoreland, P. R. *Symp. (Int.) Combust. [Proc.] 21st* **1986**, 773.
(16) Thomas, S. D. Ph.D. Thesis, University of Massachusetts, Department of Chemical Engineering, 1992.
(17) Timonen, R. S.; Russell, J. J.; Sarzynski, D.; Gutman, D. *J. Phys. Chem.* **1987**, *91*, 1873.
(18) Slagle, I. R.; Gutman, D. *J. Am. Chem. Soc.* **1985**, *107*, 5342.
(19) Donaldson, D. J.; Leone, S. R. *J. Phys. Chem.* **1987**, *91*, 3128.
(20) Young, M. A.; Pimentel, G. C. *J. Phys. Chem.* **1990**, *94*, 4884.
(21) It is presumed that reaction 2 is $\approx 5 \text{ kJ mol}^{-1}$ more exothermic than reaction 3 based on the differences in the resonance energies of C_3H_3 and C_3H_5 , as well as a 4 kJ mol^{-1} difference in reaction enthalpies of the $C_3H_3 + Cl_2 \rightarrow C_3H_3Cl + Cl$ and $C_3H_5 + Cl_2 \rightarrow C_3H_5Cl + Cl$ reactions. The heat of formation of C_3H_3Br is not measured which prevents direct calculation of the enthalpy change of reaction 3.
(22) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Supplement No. 1.
(23) Tsang, W. *J. Am. Chem. Soc.* **1985**, *107*, 2872.
(24) Tschuikow-Roux, E.; Chen, Y. *J. Am. Chem. Soc.* **1989**, *111*, 9030.
(25) Russell, J. J.; Seetula, J. A.; Senkan, S. M.; Gutman, D. *Int. J. Chem. Kinet.* **1988**, *20*, 759. Dobis, O.; Benson, S. W. *Int. J. Chem. Kinet.* **1987**, *19*, 691.
(26) Russell, J. J.; Senkan, S. M.; Seetula, J. A.; Gutman, D. *J. Phys. Chem.* **1989**, *93*, 5184.
(27) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Supplement No. 1.
(28) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.
(29) Tschuikow-Roux, E.; Paddison, S. *Int. J. Chem. Kinet.* **1987**, *19*, 15.
(30) Miyokawa, K.; Tschuikow-Roux, E. *J. Phys. Chem.* **1992**, *96*, 7328.
(31) Pedley, J. B.; Naylor, R. D.; Kirley, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: 1986; p 7.
(32) Kudchadker, S. A.; Kudchadker, A. P. *J. Phys. Chem. Ref. Data* **1978**, *7*, 1285.
(33) Bickerton, J.; Minos da Piedade, M. E.; Pilcher, G. *J. Chem. Thermodyn.* **1984**, *16*, 661.
(34) Tschuikow-Roux, E.; Faraji, F.; Paddison, S.; Niedzielski, J.; Miyokawa, K. *J. Phys. Chem.* **1988**, *92*, 1488.
(35) Mendenhall, G. D.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1973**, *77*, 2707.
(36) Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 7734.
(37) Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 2969.
(38) Alfassi, Z. B.; Benson, S. W. *Int. J. Chem. Kinet.* **1973**, *5*, 879.
(39) Krech, R. H.; McFadden, D. L. *J. Am. Chem. Soc.* **1977**, *99*, 8402.
(40) Landolt-Börnstein, *Zahlenwerte und Funktionen*; Springer-Verlag: Berlin, 1951; Atom und Molekular Physik, Vol. 1, Part 3, p 509.