

flow rate of P into the VLPP reactor (in units of molecules $s^{-1} L^{-1}$). With the use of (A-4)–(A-6), (RH) can be expressed as a function of (HX):

$$(RH) = \frac{k_a}{k_e^{RH}} (R\cdot)(HX) = \frac{k_a}{k_e^{RH}} \frac{R_R^i}{k_e^{R\cdot} + k_a(HX)} \times \frac{R_{HX}^i}{k_e^{HX} + k_a(R\cdot)} \quad (A-7)$$

(A-7) is simplified to give (A-8) under the condition $(HX) \gg (R\cdot)$:

$$(RH)_\infty = \frac{k_a}{k_e^{RH}} \frac{R_R^i}{k_a(HX)} \frac{R_{HX}^i}{k_e^{HX}} \quad (A-8)$$

With the definition $1/f = (RH)_\infty / (RH)$, the following expression is obtained, where $R^{\circ}_{HX} = k_e^{HX}(HX)$:

$$1/f = 1 + \frac{k_e^{R\cdot} k_e^{HX}}{k_a R^{\circ}_{HX}} + \frac{R_R^i}{R^{\circ}_{HX}} \quad (A-9)$$

In the limit of high (HX), where $R^i_{HX} = R^{\circ}_{HX}$ holds to a good approximation and where R_R^i is negligible with respect to R°_{HX} and R^i_{HX} , respectively, (A-9) can be simplified to expression (A-10), which relates the experimental quantities $1/f$ and R^i_{HX} to the desired rate constant k_a if the escape rate constants $k_e^{R\cdot}$ and k_e^{HX} are known.

$$1/f = 1 + \frac{k_e^{R\cdot} k_e^{HX}}{k_a R^i_{HX}} \quad (A-10)$$

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- (15) This assumption results in the following relations:⁶ $E_{d,o} = \Delta E^{\circ}_o$; $\Delta E_o^{\circ T} = \Delta E^{\circ}_o + T(\Delta C_v)$, where $E_{d,o}$ is the critical energy for the bond-breaking reaction.

Direct Measurement of Absolute Rates of Hydrogen Abstraction by *tert*-Butoxy Radicals. A Flash Photolysis Electron Spin Resonance Study

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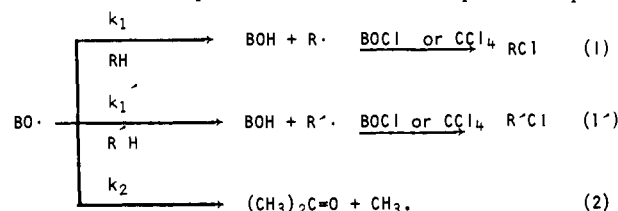
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Abstract: The flash photolysis electron spin resonance spectroscopy is applied to direct monitoring of the growth of the product radicals from the hydrogen abstraction reaction to obtain the rate constant. Photolysis of di-*tert*-butyl peroxide is the source of *tert*-butoxy radicals. Cyclopentane, anisole, methyl *tert*-butyl ether, and methanol as hydrogen atom donors have been studied: the Arrhenius parameters $\log A$ ($M^{-1} s^{-1}$) and activation energy E_a (kcal/mol) per active hydrogen have been determined to be 9.1 and 6.1, 8.8 and 5.9, 8.8 and 5.2, and 8.6 and 5.3, respectively. The absolute rates (20 °C) are about a factor of 1.5 higher than the previous (indirect) estimates, but about a factor of 2 lower than a recent study by Scaiano et al. using optical laser flash photolysis.

This work was initiated for two major goals: (1) the production of radicals for CIDEP (chemically induced dynamic electron polarization) studies^{1,2} by the photochemical decomposition of di-*tert*-butyl peroxide³ (BOOB) and (2) the measurement of absolute rate constant of hydrogen abstraction reaction by *tert*-butoxy radicals (BO \cdot). We failed to observe any CIDEP effect in the systems studied, but we were fortunate enough to be able to measure the absolute rate constants of some of the hydrogen abstraction reactions of BO \cdot . Our method represents a more direct way than previously reported to measure these rate constants, which are still hard to come by.^{4,5}

In 1960 Walling started reporting a series of a well-planned and elegant investigations on the rate of hydrogen abstraction reactions by *tert*-butoxy radicals.⁶ A very large amount of relative rate constants have since been determined. The basic reaction used was the well-known radical chlorination of hy-

drocarbons by *tert*-butyl hypochlorite (BOCl). Relative reactivities of organic compounds toward BO \cdot (k_1/k_1') may be measured in competitive experiments where two substances (RH and R'H) react with BO \cdot and the product radicals then form products such as organic chlorides by reaction with hypochlorite (or carbon tetrachloride if other initiators of BO \cdot are used). See eq 1, 1', and 2. The ratio of rate constants k_1/k_1' may be determined by estimating the relative yields of RCl and R'Cl or the consumption of reactants in competitive experi-



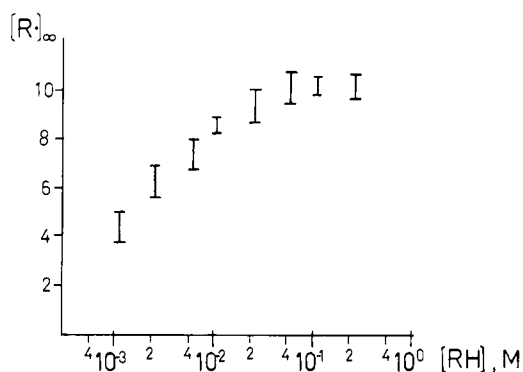


Figure 1. Plot of $[R]_{\infty}$ vs. $[RH]$ to test and to obtain the condition that almost all of $BO\cdot$ radicals are converted to $R\cdot$. In this plot RH is cyclopentane. Vertical scale at 10 is equivalent to 1.04×10^{-6} M.

ments. The relative rate may be determined indirectly by comparing BOH /acetone ratios on reaction with each substrate using reaction 2 as an internal clock. In order to put these rate constants on an absolute basis, Ingold and his collaborators,⁷ as well as Walling and Kurkov⁸ set out to determine the rate constant of some reactions absolutely so that the large bulk of relative rate constant could be translated into absolute rate constants. They both chose toluene as a standard RH . Unfortunately there was quite a large discrepancy (a factor of 10) in the rate constants between these two reports, particularly in view of the high accuracy among the relative rate constants. Part of the reason is due to the rather complicated analysis of the total reaction mechanism.

Recently Lorand and Wallace⁹ applied a competition technique to the decompositions of *tert*-butyl triphenylperacetate and *tert*-butyl 2,2-diphenyl-3,3-dimethylperbutanoate to obtain the absolute rate constant for the reaction of *tert*-butoxy radicals with toluene. A value of $\sim 0.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C in toluene was deduced. However, the authors conceded that there were some important but untested (or difficult to test) assumptions in deriving this rate constant. Even so this is still the most reliable value to date.⁴

Experimental Section

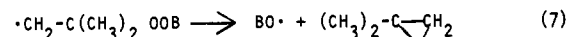
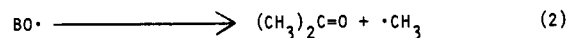
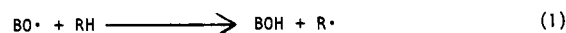
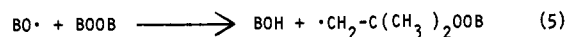
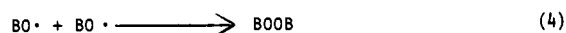
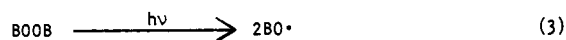
The general principle and techniques of flash photolysis electron spin resonance (FPESR) have been described by Bolton and Warden.¹⁰ The system used at the Photochemistry Unit has been further improved. The time resolution of the system is $\sim 0.3 \mu\text{s}$ using a direct-detection without magnetic field modulation.¹¹ Because of the lack in CIDEP sensitivity enhancement in these experiments, the low sensitivity of direct detection inhibited its use for the ordinary kinetic studies. The original 100-kHz field modulation on the Varian E-12 X-band ESR spectrometer was then employed, but the time response of the system has been improved to $\sim 30 \mu\text{s}$ by widening the band pass in the "low pass filter". The pulsed light sources used (Model 610) were developed here at the Photochemistry Unit and are now manufactured by Photochemical Research Associate Inc. One light source had half-width of $1.5 \mu\text{s}$ and the other one $20 \mu\text{s}$. A Nicolet 1072 computer of average transient coupled with a Biomation 610B transient recorder was used for collecting and averaging data. For this work 126–512 transients were required for an analyzable ESR kinetic curve. The sample temperature was controlled within ± 2 °C during a run. Di-*tert*-butyl peroxide (K&K) was initially passed through alumina to remove possible traces of hydroperoxide prior to use. However, controlled experiments showed that the purification had no significant effect on these studies. Cyclopentane and anisole were distilled before use. Other chemicals were of highest purity commercially available and used as received. Pure BOOB or its mixture with benzene was used as solvent. There were no significant differences within the experimental error ($\pm 20\%$) found between pure BOOB and 1:4 v/v BOOB–benzene as solvent. The sample solutions contained in 4-mm-o.d. Suprasil tubes were deoxygenated by purging with nitrogen and the tubes were then sealed off. Two to four kinetic curves were obtained for each sample depending on the initial concentration

of RH , the concentration of $BO\cdot$ per flash, and the number of transients required for such a curve. The ESR amplitude was always optimized to give the largest signal-to-noise ratio. Most of the kinetic curves were obtained on the largest peaks in the spectra so as to achieve higher signal-to-noise ratio and to avoid possible CIDEP effect, even though they were not detected in this study. Radical concentrations were calibrated with standard pitch samples, which were in turn standardized against weighed DPPH in benzene. The pitch samples contained in a melting-point capillary tube were immersed in the same solvents (BOOB or BOOB–benzene mixture) in the same 4-mm tube to minimize the change in Q of the cavity. The power saturation for standard calibration of concentration was always avoided. When high microwave power was used to optimize the signal-to-noise ratio in a kinetic run, the concentration was internally calibrated. It should, however, be noted that the absolute concentration of radicals has no direct consequence in the rate measurement if the kinetic is first order or pseudo first order.

Method and Reaction Scheme

To avoid the complicated analysis of the overall reaction mechanism involved in the previous studies, the flash photolysis electron spin resonance (FPESR) technique was employed to isolate the interesting elementary reaction for study. Although the technique is rather straightforward and general, the ESR time resolution and signal sensitivity limit the accuracy of the measurement to not better than $\pm 20\%$.

Reactions 1–8 have been considered in the reaction scheme to study the hydrogen abstraction reaction by $BO\cdot$ to obtain rate constants.



The production of $BO\cdot$ radicals is effected by a pulse of light from the photodecomposition of BOOB and considered to be instantaneous with respect to the hydrogen abstraction reaction. Since $BO\cdot$ is believed not to be detected by ESR,¹² the rate of hydrogen abstraction reaction is monitored from the production of alkyl radicals. The rise time (half-life) should be adjusted to be longer than $50 \mu\text{s}$ within instrument time resolution by varying the concentration of RH or the temperature.

Results and Discussion

Cyclopentane was first chosen for study partly because the cyclopentyl radical generated by radiolysis was the first alkyl radical system showing strong CIDEP phenomenon¹³ and partly because this substrate is in common use as a reactivity standard for ESR studies of $BO\cdot$ radicals.¹⁴ The cyclopentyl radical¹⁵ generated from hydrogen abstraction by $BO\cdot$ from cyclopentane in the present study did not show any significant deviations from thermal equilibrium either under the steady-state irradiation or under a pulse kinetic study. The failure to observe CIDEP effect from these BOOB + RH systems is in fact an advantage in the kinetic study for hydrogen abstraction because the thermal equilibrium guarantees a simple measurement of radical concentration.

Because of several possible competitive reactions (reactions 2, 4, 5, and 6), we must convince ourselves experimentally that the rise of $R\cdot$ provides a true measure of the rate of reaction 1. From the reaction scheme, it is expected that reaction 1 could

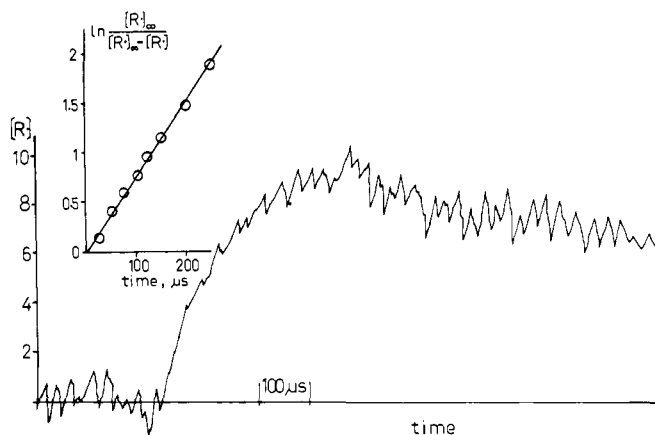


Figure 2. Time-dependence trace of ESR signal of $C_6H_5OCH_2$ radicals in FPESR. The concentration of anisole in BOOB was 9.5×10^{-2} M. The upper curve is the corresponding pseudo-first-order plot $\{\ln [R]_{\infty} / ([R]_{\infty} - [R])\}$ vs. time.

Table I. Rate Constants^a for Hydrogen Abstraction Reaction of *tert*-Butoxy Radicals at 293 K

substrate	k_1/M^{-1} $s^{-1} \times 10^{-4}$	k_1/M^{-1} $s^{-1} \times 10^{-4}$ per active H	$k_1(\text{expt})/$ $k_1(\text{lit.})^b$
cyclopentane	34 ^c	3.4 (1.94) ^d	1.75
anisole	7.2	2.4 (1.76)	1.36
methyl <i>tert</i> -butyl ether	24.3	8.1 (5.3)	1.53
methanol	12.9 ^c	4.3 (—) ^e	—

^a Recalculated from the Arrhenius parameters of Table II.

^b $k_1(\text{expt})$ and $k_1(\text{lit.})$ are values of this work and from literature, respectively. ^c Paul, Small, and Scaiano^{5b} have reported k_1 values for cyclopentane and methanol at 295 K to be $8.8 \times 10^5 M^{-1} s^{-1}$ and $2.9 \times 10^5 M^{-1} s^{-1}$, respectively. ^d Values in parentheses are literature values taken from ref 16. ^e A value of $8.8 \times 10^4 M^{-1} s^{-1}$ was reported by D. H. Ellison, G. A. Salmon, and F. Wilkinson, *Proc. R. Soc., Ser. A*, **328**, 23 (1972), for the reaction $CH_3O \cdot + CH_3OH \rightarrow CH_3OH + \cdot CH_2OH$.

dominate over reactions 2, 4, 5, and 6 for the decay of $BO\cdot$ radicals if the concentration of RH is large enough. That is, under such a concentration of RH, the photolytically produced $BO\cdot$ will react only with RH to produce $R\cdot$ in a one-to-one correspondence. Figure 1, a plot of $[R]_{\infty}$ vs. $[RH]$, shows how this condition can be achieved. In these experiments the flash energy per pulse was kept identical to assure that the initial $BO\cdot$ concentration, $[BO\cdot]_0$, was the same for valid comparison. $[R]_{\infty}$ indeed reaches a plateau as expected when $[RH]$ increases indicating that almost all of $BO\cdot$ converts into $R\cdot$. In this particular case >90% conversion is achieved when the concentration of cyclopentane is equal to above 2×10^{-2} M. The values of $[R]_{\infty}$ were obtained from the flash kinetic ESR curve as shown in Figure 2. When the initial concentration of $BO\cdot$ was decreased by allowing less light into the sample, the plateau in Figure 1 was reached (not shown) at a lower concentration of RH. This shift of RH concentration in reaching the plateau with the different initial $BO\cdot$ concentration may be taken to mean that the recombination of two $BO\cdot$ radicals, reaction 4, is the major competitor with reaction 1, because this is the only second-order reaction with respect to $BO\cdot$ in the scheme. We therefore believed and worked on the assumption that where the $[R]_{\infty}$ is near (>90% of the plateau value) the plateau indicates that reaction 1 is the only major reaction responsible for the decay of $BO\cdot$. To satisfy the above condition readily the initial concentration of $BO\cdot$ did not exceed 2×10^{-6} M; most of them in this study were in fact lying between 8×10^{-7} M and 1.5×10^{-6} M by controlling the light flash.

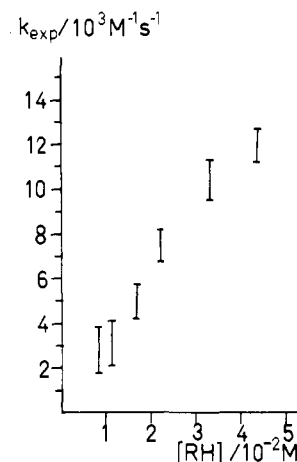


Figure 3. Plot of the experimental first-order rate constant vs. the concentration of RH (cyclopentane) at 293 K.

Table II. Arrhenius Parameters for Hydrogen Abstraction by *tert*-Butoxy Radicals (per Active Hydrogen)

substrate	$\log A,^a$ $M^{-1} s^{-1}$	$E_a,^a$ kcal/mol
cyclopentane	9.1 (9.2) ^b	6.1 (6.56) ^b
anisole	8.8 (8.7)	5.9 (5.95)
methyl <i>tert</i> -butyl ether	8.8 (8.7)	5.2 (5.31)
methanol	8.6 (—)	5.3 (—)

^a The errors in $\log A$ and E_a are ± 0.2 and ± 0.3 kcal/mol, respectively. ^b Values in parentheses are taken from ref 16.

Under this working assumption the time dependence of ESR signals of $R\cdot$ (Figure 2) should follow the kinetic equation

$$-d[BO\cdot]/dt = d[R\cdot]/dt = k_1[BO\cdot][RH] = k_1\{[R]_{\infty} - [R\cdot]\}[RH]$$

Indeed analysis of the rise provides a reasonable first-order kinetic ($\ln [R]_{\infty} / \{[R]_{\infty} - [R\cdot]\}$ vs. time) ascribed to reaction 1. Rate constants k_1 were calculated from the slope and the RH concentration. The rate constants k_1 determined from curves like those in Figure 2 were shown to be independent (with an error of $\pm 20\%$) of RH concentrations in all four substrates. The case of cyclopentane was shown in Figure 3. The range of RH concentrations was, however, limited to only a factor of 3 or 4. Higher concentrations would increase the pseudo-first-order reaction rate not measured reliably by the present setup. On the other hand lower concentrations would require lower $BO\cdot$ initial concentrations to place $[R]_{\infty}$ close to the plateau region and this lower $BO\cdot$ initial concentration would in turn reduce the ESR signals to obtain a reasonable k_1 measurement.

The absolute rate constants for hydrogen abstraction reaction of $BO\cdot$ radicals with cyclopentane, methanol, methyl *tert*-butyl ether, and anisole at room temperature (293 K) are summarized in Table I. The corresponding Arrhenius parameters are collected in Table II. The temperature range was from 253 to 303 K. A typical example of the Arrhenius plot is shown in Figure 4. Though direct measurement for these four substrates was not previously reported, the absolute rate constants could be calculated from the relative rate constants with respect to the standard absolute measurement for toluene. A critical review of several common hydrogen abstraction reactions in solution has recently been reported by Hendry et al.¹⁶ Their relevant estimates are reproduced in Table I and Table II for comparison, whereas the related data for methanol were apparently never reported. The standard absolute values for toluene at 273 and 313 K of 0.87×10^4 and $3 \times 10^4 M^{-1} s^{-1}$,

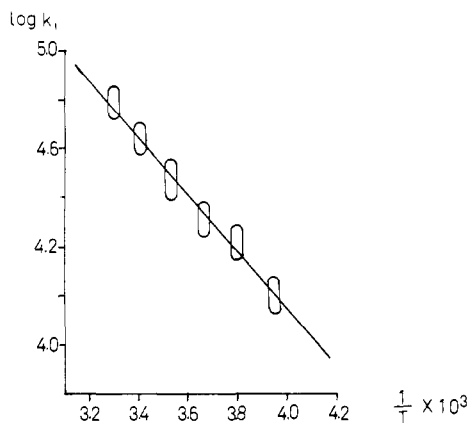


Figure 4. Arrhenius plot for the reaction $\text{BO}\cdot + \text{CH}_3\text{OH} \rightarrow \text{BOH} + \text{CH}_2\text{OH}$.

respectively, were used in their calculation.¹⁷ The activation energies were calculated from a rate constant and assigned values of $\log A$. The assignments of $\log A$ were based on an analysis of Benson.¹⁸ They also estimated that these values were accurate within ± 0.5 in $\log A$, equivalent to a factor of 3 in k_1 . As a matter of fact the Arrhenius parameters for some hydrocarbons have been estimated from experiments where the variation in k_1/k_2 with temperature was measured.¹⁹⁻²² However, there were no reliable values for k_2 ¹⁶ and therefore this method could not be reliably applied.

Comparison of the values of the present study with those of the "literature" values¹⁶ is surprisingly close in view of the rather larger errors involved in the present measurements and the semiempirical assignment of $\log A$ in the "literature" values. Our results at 293 K, however, were generally higher (see Table I), and an average of a factor of 1.55 was determined. The factor is beyond the experimental errors (reproducibility) but is not at all unreasonable because the controversy and uncertainty of k_1 , which exists in the literature as well as the best literature estimates are only good within a factor of 3.

It was, however, pleasing to learn during the preparation of this manuscript that a new absolute rate determination of $\text{BO}\cdot$ with diphenylmethanol and cumene using nanosecond laser flash photolysis techniques was reported in this journal by Small and Scaiano⁵ (denoted as SS for later discussion). Values of 6.9×10^6 and $8.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ were determined, respectively. The rate for cumene is at least three times higher than could be expected from the highest values previously estimated.¹⁶ While the authors did not explain this large discrepancy, they pointed out that these values compared well with the values for the benzophenone triplet of 5.5×10^5 for cumene and $8.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for diphenylmethanol. This striking similarity of benzophenone triplets and $\text{BO}\cdot$ radicals in hydrogen abstraction was first noted by Padwa²³ and by Walling and Gibian.²⁴

If our results are compared with those of SS through the bridge of toluene, then our results are about a factor of 2 smaller than theirs.²⁵ The discrepancy may better be understood after the two techniques are compared.

The basic idea of each technique, including the use of the photolysis of BOOB as the source of $\text{BO}\cdot$ radicals, is very similar if not identical. Both methods could not directly detect $\text{BO}\cdot$ radicals but rather monitored the product radical $\text{R}\cdot$ instead. The advantages and disadvantages of both optical detection and ESR detection in flash photolysis have been discussed in detail elsewhere.¹⁰ We just comment on several points relevant to SS work and ours. Their method encompassed a much higher sensitivity and much better time resolution ($< 1 \mu\text{s}$) and therefore they could study RH concentration depen-

dence in a wider range, but simple alkyl radicals do not provide a suitable electronic absorption for detection as pointed out in their paper whereas ESR detection is easy. Therefore most substrates of interest could not be studied optically directly, but they apparently, following the concentration of the diphenylhydroxymethyl radical in a system containing both diphenylmethanol and the second substrate, solved the problem by a kind of competitive method. Another point is that it is easier to carry out a temperature dependence study in the FPESR. Our time domain (half-times) was between $\sim 60 \mu\text{s}$ and $\sim 250 \mu\text{s}$ while theirs was between $\sim 200 \text{ ns}$ and $2 \mu\text{s}$. This difference has some important implications, because reaction 7 may have different roles to play in these two distinct time domains. Reaction 7 plays a central role in the decomposition of BOOB in the pure state, thermally or photochemically, as suggested by Bell, Rust, and Vaughan,²⁶ who identified oxirane (isobutylene oxide) as a new major product, not found in other solvents such as cumene and *tert*-butylbenzene. Later Bloodworth et al.²⁷ confirmed that β -peroxyalkyl radicals are precursors of oxirane and also determined k_7 , by competition of ring closure with radical reduction by tin hydride, to be $\sim 7 \times 10^5 \text{ s}^{-1}$ at 25 °C. Reaction 7 was totally ignored by SS,²⁸ while this rapid decay of β -peroxyalkyl radicals to regenerate $\text{BO}\cdot$ could help to minimize the interference of reaction 5 in our time domain. SS assigned a first-order component of the $\text{BO}\cdot$ reaction in their measurement of the rate constant of hydrogen abstraction from diphenylmethanol to reaction 5, k_5 (per hydrogen), being equal to or less than $8.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at 22 °C. However, our present ESR kinetic studies together with steady-state ESR studies in our and other laboratories not observing the ESR spectrum of $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OOB}$ in BOOB demand a slower hydrogen abstraction rate from BOOB and/or a faster decay rate of this radical. This is a serious discrepancy between SS and us, but we cannot offer any satisfactory explanation at the present time. With such a discrepancy in analysis of data, a difference factor of 2 in rate constants between these two measurements becomes less serious.

In conclusion it appears that the rate of hydrogen abstraction by $\text{BO}\cdot$ radicals is generally higher than previously believed. The present study also provides the first direct measurement of the Arrhenius parameters for hydrogen abstraction of $\text{BO}\cdot$. These parameters appear well behaved as expected from the analysis of general hydrogen abstraction by radicals.^{16,18} One of the important applications is to provide absolute reactivity standards for ESR studies of $\text{BO}\cdot$ radicals.

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Stabilities of Isomeric Halonium Ions $C_2H_4X^+$ ($X = Cl, Br$) by Photoionization Mass Spectrometry and Ion Cyclotron Resonance Spectroscopy. General Considerations of the Relative Stabilities of Cyclic and Acyclic Isomeric Onium Ions

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Abstract: At least two noninterconverting structural isomers of the halonium ions $C_2H_4X^+$ ($X = Cl, Br$) are shown to exist in the gas phase. Threshold measurements of their formation through halide loss and fragmentation of corresponding dihaloethanes yield enthalpies of formation for these species. For $X = Cl$, the cyclic halonium ion is 5.6 kcal/mol less stable than the acyclic species CH_3CHCl^+ . These stabilities are reversed for $X = Br$, with the cyclic isomer being more stable by 1.4 kcal/mol. In addition, relative stabilities of a larger class of onium ions are inferred from ion cyclotron resonance studies of exchange reactions between $C_2H_4X^+$ and HY to give $C_2H_4Y^+$ and HX ($X, Y = Cl, Br, OH, SH, NH_2, PH_2$). From the preferred direction of these processes, stability is inferred to increase in the order $X = OH < Cl < Br < SH, PH_2 < NH_2$ for the cyclic onium ions and $X = Cl < Br < SH, PH_2 < OH < NH_2$ for their acyclic isomers.

Introduction

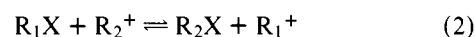
The study of chemical reaction dynamics abounds with hypothetical intermediates which are convenient constructs based more on intuition than fact. With structures and properties inferred from related stable molecules and theoretical calculations, these species justify a myriad of observed kinetic phenomena. More recently, however, development of sophisticated instrumentation and novel experimental conditions have permitted many of these transients to be observed and characterized directly. For example, Roberts and Kimball² in 1937 proposed a cyclic bromonium ion intermediate to account for observed trans stereospecificity in addition of bromine to alkenes. Halonium ion intermediates have been suggested by other workers also.^{3,4} In recent years these species have been investigated in both liquid and gas phase by a variety of techniques, including nuclear magnetic resonance,^{5,6} ion cyclotron resonance (ICR),^{7,8} and conventional mass spectrometry.⁹⁻¹³ Theoretical studies have also been reported.^{14,15} Among the more interesting questions addressed by these studies are considerations of the existence and relative stabilities of structural isomers of onium ions.

Several means exist to compare the stabilities of isomeric and congeneric onium ions. In the case of structural isomers, relative stabilities can be inferred directly from heats of for-

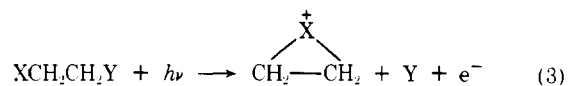
mation. Halide and hydride affinities defined by



(where $X^- = \text{halide ion or } H^-$) are also useful for comparing ion stabilities. Using eq 1 the stabilities of onium ions (as Lewis acids) can be compared with a common reference base. Relative stabilities can be inferred from studies of halide and hydride transfer reactions as generalized in the equation



In the present study we report detailed investigations of several small halonium ions $C_2H_4X^+$ ($X = Cl, Br$). Heats of formation are determined from photoionization mass spectrometric (PIMS) threshold measurements of reactions 3 and 4. Further, experiments are discussed that demonstrate the



existence of two unique structural isomers, assumed to be the acyclic and cyclic species I and II, which yield different reaction products in mixtures containing NH_3 . The isomers do not