J. Am. Chem. Soc. **1994**, *116*, 7872–7876

Reaction Mechanism of Hydrogen Abstraction by the Bromine Atom in Water

Gábor Merényi* and Johan Lind

Contribution from the Department of Chemistry, Nuclear Chemistry, Royal Institute of Technology, 10044 Stockholm, Sweden

Received February 28, 1994[⊗]

Abstract: By means of pulse radiolysis, bromine atoms were generated during one-electron reduction of 1,2-dibromoethane in water. Rate constants of hydrogen abstraction reactions between the bromine atom and several hydrogen donors, RH, were determined using Br^- and promethazine as monitor substances. Comparison of the aqueous rate constants with those measured in acetonitrile and some alcohols reveals the hydrogen abstraction rate to be largely unaffected by the polarity of the solvent. In particular, the reaction does not utilize the potential rate enhancement that would result were the free energy gain of HBr dissociation in water to lower the transition state. Thus, the rate-determining step of the reaction seems to produce molecular HBr. For a number of oxygen-containing organic substrates, the aqueous rate constants were found to display an excellent linear correlation with the equilibrium constants of the hydrogen abstraction reactions. However, at similar thermochemistry, the rates for alkanes are significantly lower than those for alcohols and similar heteroatomics. This was interpreted in terms of a polar transition state, where the ionization potential of the radical, $R^\bullet$, is an important parameter. During one-electron reduction of 1,2-dibromoethane by the hydrated electron, some $Br_2^{\bullet-}$ was found to form even in the presence of high concentrations of $Br^\bullet$ atom scavengers. This fact was utilized for the determination of the rate constant of decay of $Br_2^{\bullet-}$ into $Br^\bullet$ and Br^- ($1.9 \times 10^4\ s^{-1}$). By means of this rate constant, the equilibrium constant for $Br^\bullet + Br^- \rightleftharpoons Br_2^{\bullet-}$ was revised to $6 \times 10^5\ M^{-1}$, resulting in $E^\circ(Br^\bullet/Br^-) = 1.96$ V vs NHE.

Introduction

The bromine atom has long been utilized in gaseous hydrogen atom abstraction reactions in order to determine X–H bond strengths in various compounds.[1] This feverish activity in the gas phase has not been paralleled in fluid solution. Thus, apart from some exceptions, the absolute reactivity of Br in the condensed phase has largely remained *terra incognita*. In contrast, the study of the selectivity of bromine atoms in hydrogen abstraction reactions in solution has been accorded much attention. Some conclusions drawn from such studies follow. The rate of $Br^\bullet$ toward alkyl and aralkyl C–H bonds[2] is in the order 1° ≪ 2° ≪ 3°. Benzylic compounds react with $Br^\bullet$ much more readily than do their alkylic analogues. Introduction of a heteroatom enhances the rate of hydrogen abstraction. Thus, benzyl methyl ethers are much more reactive than alkylbenzenes.[3] The effect of substituent on the rate of $Br^\bullet$ reacting with benzylic compounds varies with the type of benzylic C–H bond, as reflected in ρ values ranging[3–7] from −1.38 for toluenes to −0.12 for dibenzyl ethers.

The few absolute reactivities mentioned above refer to a study of $Br^\bullet$ in methanol,[8] a number of hydrogen abstraction reactions in water,[9,10] and recently some hydrogen abstraction reactions in acetonitrile.[11] There has also appeared a paper[12] that specifically addresses bromine atom reactions with polyunsaturated fatty acids (PUFA) in water/*tert*-butyl alcohol mixtures. In this work we shall inquire more systematically into the factors that influence the rates of such reactions in water and, to a lesser extent, also in other solvents.

Experimental Section

Pulse radiolysis was performed at room temperature utilizing doses of 2–15 Gy/pulse corresponding to 1.2×10^{-6}–9×10^{-6} M of radicals. The 7-MeV microtron accelerator[13] and the computerized optical detection system[14] have been described elsewhere. Dosimetry was performed by means of an aerated 10^{-2} M KSCN solution, taking[15] $G\epsilon = 2.23 \times 10^4$ $100eV^{-1}\ M^{-1}\ cm^{-1}$ at 500 nm. The solutions were made up in Millipore deionized water. The solutions were purged by argon, and they contained 5×10^{-3}–1×10^{-2} M 1,2-dibromoethane, sufficient to capture all e^-_{aq} in the presence of the substrates RH. When necessary, 0.1 M *tert*-butyl alcohol was added to scavenge the $OH^\bullet$ radicals. The concentration ranges of the substrates and the assorted monitors (3×10^{-5}–5×10^{-5} M) employed were as follows: methanol, 0–5 M, promethazine; ethanol, 2-propanol, formaldehyde, 0–1.5 M, Br^- and promethazine; HCO_2^-, 0–1.5 $\times 10^{-3}$ M, Br^-; acetaldehyde, 0–6 $\times 10^{-3}$ M, Br^- and promethazine; *t*-BuOH 0–100%, promethazine; adipinic acid disodium salt, 0–1 M, promethazine; L-lactate, glycolate, 0–0.05 M, Br^-. 4-Iodophenol (0–10^{-4} M) was monitored directly by the absorbance of the 4-iodophenoxyl radical.

Chemicals: 1,2-dibromoethane (99%), 1,2-diiodoethane (99%), 2-propanol (HPLC grade), NaN_3 (99%), NaBr (99.99%), KI (99%), HCO_2Na (99+%), NaOH (99.99%), acetaldehyde (99%), L-lactic acid sodium salt (99%), glycolic acid (99%), 4-iodophenol (99%), formaldehyde (reagent grade), and promethazine hydrochloride (98%) were all from

---

[⊗] Abstract published in *Advance ACS Abstracts*, July 15, 1994.

(1) See, e.g.: McMillen, D. F.; Golden, D. M. In *Annual Review of Physical Chemistry*; Rabinovitch, B. S., Schurr, J. M., Strauss, H. L., Eds.; Annual Reviews Inc.: Palo Alto, CA, 1982; Vol. 33, pp 493–532 and references therein.

(2) Russel, G. A., In *Free Radicals, Volume 1*; Kochi, J. K., Ed.; John Wiley: New York, 1973; pp 275–332 and references therein. Poutsma, M. L. In *Free Radicals, Volume 2*; Kochi, J. K., Ed.; John Wiley: New York, 1973; pp 159–229 and references therein.

(3) Huang, R. L.; Lee, H. H.; Malhotra, M. S. *J. Chem. Soc.* **1964**, 5963.

(4) Walling, C.; Rieger, A. L.; Tanner, D. D. *J. Am. Chem. Soc.* **1963**, *85*, 3129.

(5) Martin, M. M.; Gleicher, G. J. *J. Org. Chem.* **1963**, *28*, 3266.

(6) Friedrich, S. S.; Andrews, L. J.; Keefer, R. M. *J. Org. Chem.* **1970**, *35*, 944.

(7) Huang, R. L.; Lee, H. H.; Malhotra, M. S. *J. Chem. Soc.* **1964**, 5951.

(8) Lilie, J.; Koskikallio, J. *Acta. Chem. Scand., Ser. A* **1984**, *38*, 41.

(9) Lind, J.; Merényi, G. In *Proceedings of the Seventh Tihany Symposium on Radiation Chemistry*; Dobó, J., Nyikos, L., Schiller, R., Eds.; Hungarian Chemical Society: Budapest, 1991; pp 185–190.

(10) Lind, J.; Jonsson, M.; Shen, X.; Eriksen, T. E.; Merényi, G.; Eberson, L. *J. Am. Chem. Soc.* **1993**, *115*, 3503.

(11) Scaiano, J. C.; Barra, M.; Krzywinski, M.; Sinta, R.; Calabrese, G. *J. Am. Chem. Soc.* **1993**, *115*, 8340.

(12) Guha, S. M.; Schöneich, C.; Asmus, K.-D. *Arch. Biochem. Biophys.* **1993**, *305*, 132.

(13) Rosander, S. Ph.D. Thesis. The Royal Institute of Technology, Stockholm, Sweden, 1974; TRITAEEP-74-16, p 28.

(14) Eriksen, T. E.; Lind, J.; Reitberger, T. *Chem. Scr.* **1976**, *10*, 5.

(15) Fielden, E. M. In *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*; Baxendale, J. H., Busi, F., Eds.; Nato Advanced Study Institutes Series; Reidel: Dordrecht, Holland, 1982; pp 49–62.

0002-7863/94/1516-7872$04.50/0

Aldrich; methanol (Merck p.a.), ethanol (Vin & Spritcentralen, 96% p.a.), 2-methyl-2-propanol (Merck p.a.), and H_2SO_4 (Merck suprapure) were used as received.

Results and Discussion

Generation of Br• Atoms from 1,2-Dibromoethane. In ref 16 it was established that, upon one-electron reduction of 1,2-dibromoethane by the hydrated electron in water ($k_1 = 1.2 \times 10^{10}$ M^{-1} s^{-1}, ref 17), Br^- production in reaction 1 is followed by the expulsion of Br• (reaction 2).

$$e^-_{aq} + BrCH_2CH_2Br \rightarrow BrCH_2CH_2^{\bullet} + Br^- \qquad (1)$$

$$BrCH_2CH_2^{\bullet} \rightleftharpoons CH_2CH_2 + Br^{\bullet} \qquad (2)$$

In addition, the rate constant k_2 in water was measured[16] to be 2.8×10^6 s^{-1}. In *tert*-butyl alcohol/water mixtures, a somewhat lower rate constant, $k_2 \approx 6 \times 10^5$, was observed.[12] Later, the expulsion of Br• subsequent to photochemical dissociation of $BrCH_2CH_2Br$ into $BrCH_2CH_2^{\bullet}$ and Br• in acetonitrile was demonstrated.[11] At the same time, the rate constant of reaction 2, k_2 in that solvent, was shown to exceed 5×10^7 s^{-1}. These discordant values prompted us to reevaluate k_2. By measuring the rate of absorbance buildup of the promethazinium radical cation in water as a function of the added concentration of promethazine (10-(2-(dimethylamino)propyl)phenothiazine), we obtained a limiting rate of $(3.8 \pm 0.3) \times 10^6$ s^{-1}, which we interpret as k_2. This is very close to although somewhat higher than the value reported in ref 16. In light of these findings, we speculate that the very high value for k_2 observed in ref 11 might bear on some vibrational excitation of $BrCH_2CH_2^{\bullet}$, it having been generated photochemically.

Previously, Skell et al.[18] concluded, on kinetic grounds, that the $BrC_2H_4^{\bullet}$ radical in organic solvents (and thus most probably in the gas phase, as well) is stabilized by ca. 3 kcal/mol as compared to the ethyl radical. This extra stability, i.e., BDE($H\text{-}CH_2CH_3$) − BDE($H\text{-}CH_2CH_2Br$), is a result of Br bridging. Combining our k_2 in water with the best value of k_{-2} in the gas phase,[19] i.e., $(1 \pm 0.4) \times 10^8$ M^{-1} s^{-1}, we obtain $K_2 \approx 0.04$ M. We can also calculate a fictitious K_2' that would apply were the C–H bond in $H\text{-}CH_2CH_2Br$ equally strong as in ethane (101.2 kcal/mol), i.e., if $BrC_2H_4^{\bullet}$ were not stabilized at all. Modifying the data in ref 20, we obtain $K_2' = 0.6$ M. With $K_2'/K_2 = 15$, the radical stabilization energy comes out as 1.6 kcal/mol. While confirming the $BrC_2H_5^{\bullet}$ radical to be stabilized, our value is seen to be lower by ca. 1.4 kcal/mol than that of Skell et al.[18] However, quantitative agreement can be achieved on the assumption that k_2 in apolar solvents and in the gas phase may be lower than that in water by a factor of ca. 10, i.e., $\approx 4 \times 10^5$ M^{-1} s^{-1}. Such a possibility is supported by our finding that, as will be shown below, the Br• atom is destabilized by ca. 1.2 kcal/mol upon transfer from water to gas.

Direct Formation of $Br_2^{\bullet-}$. In the presence of Br^- in the solution, reactions 1 and 2 are followed by the equilibrium reaction 3 to produce the strongly absorbing $Br_2^{\bullet-}$ species with an absorbance maximum at 360 nm. However, when 1,2-dibromoethane was

$$Br^{\bullet} + Br^- \rightleftharpoons Br_2^{\bullet-} \qquad (3)$$

reduced in a Br^--free solution in the presence of 2-propanol (added in order to scavenge Br•), the prompt formation of an absorbance at 360 nm could not be suppressed. The size of the absorbance was unaffected when the concentration of 2-propanol was increased from 1 to 2 M. The spectral characteristics of the 360-nm species were found to be identical with those of $Br_2^{\bullet-}$ (produced through reaction of OH• radicals with Br^-), and this species was shown to oxidize added promethazine with the same rate[21] (6.2×10^9 M^{-1} s^{-1}) as authentic $Br_2^{\bullet-}$. This unscavengable $Br_2^{\bullet-}$ yield corresponded to ca. 35% of the e^-_{aq} initially generated, as could be confirmed from the sizes of both the $Br_2^{\bullet-}$ and the promethazinium radical cation signals. An additional support for the prompt formation of $Br_2^{\bullet-}$ comes from the following observations. In contrast to the rapid reaction of Br•, $Br_2^{\bullet-}$ was found to react much too slowly with 4-iodophenol on the pulse radiolytic time scale. When this phenol was added to solutions containing 1,2-dibromoethane, the yield of the 4– PhO• radical, deduced from its absorbance[22] at 500 nm, was only ca. 65% of that of the hydrated electrons initially formed. This indicates that reactions 1 and 2 produce Br• with only a 65% efficiency. As we also observe an absorbance at 360 nm, which corresponds to ca. 35% $Br_2^{\bullet-}$, it is clear that the latter forms simultaneously with Br•. From the disappearance of the promptly formed $Br_2^{\bullet-}$ (see Figure 1) in the presence of 1–2 M 2-propanol, the rate constant $k_{-3} = 1.9 \times 10^4$ s^{-1} is obtained, reaction −3 being the rate-determining step in the process. In an alternative approach, an Ar-purged solution containing 1 M H_2SO_4, 10^{-4} M Br_2, and 10^{-2} M methanol was pulse irradiated. Methanol was added to convert OH• radicals into •CH_2OH. An absorbance at 360 nm grew in with a rate of 5×10^5 s^{-1}, corresponding to a $Br_2^{\bullet-}$ yield of 3.4×10^{-7} M/J, the combined yields of e^-_{aq} and H•. The disappearance (Figure 1) involved rapid first-order attainment of eq 3 mixed with a slower second-order decay of $Br_2^{\bullet-}$. The dynamics was simulated numerically using the following reactions with assorted rate constants:

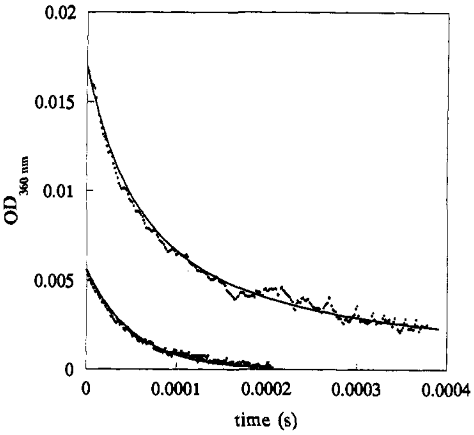

Figure 1. Decay of the absorbance at 360 nm obtained upon pulse radiolysis (dose 5.3 Gy) of argon-saturated aqueous solutions containing (lower curve) 10^{-2} M 1,2-dibromoethane and 2 M 2-propanol or (upper curve) 10^{-4} M Br_2, 1 M H_2SO_4, and 10^{-2} M MeOH. The lines are calculated using $k_{-5} = 1.9 \times 10^4$ s^{-1} (see text).

$$\text{eq 3:}\quad k_3 = 1.2 \times 10^{10}\ M^{-1}\ s^{-1}\ \text{(see below)},\qquad k_{-3} = 1.9 \times 10^4\ s^{-1}$$

$$2Br_2^{\bullet-} \rightarrow Br_2 + 2Br^- \qquad k = 2 \times 10^9\ M^{-1}\ s^{-1}\ \text{(ref 23)}$$

---

[16] Lal, M.; Mönig, J.; Asmus, K.-D. *Free Radical Res. Commun.* **1986**, *1*, 235.

[17] Lal, M.; Schöneich, C.; Mönig, J.; Asmus, K.-D. *Int. J. Radiat. Biol.* **1988**, *54*, 773.

[18] Skell, P. S.; Traynham, J. G.; James, G. *Acc. Chem. Res.* **1984**, *17*, 160.

[19] Barnes, I.; Bastian, V.; Becker, K. H.; Overath, R.; Tong, Z. *Int. J. Chem. Kinet.* **1989**, *21*, 499.

[20] Benson, S. W.; O Neal, H. E. *Natl. Stand. Ref. Data Ser.*, (*U. S., Natl. Bur. Stand.*) **1970**, *21*, 611.

[21] Bahnemann, D.; Asmus, K.-D.; Willson, R. L. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1669.

[22] Lind, J.; Shen, X.; Eriksen, T. E.; Merényi, G. *J. Am. Chem. Soc.* **1990**, *112*, 479.

[23] Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027.

$$Br_2^{\bullet -} + Br \rightarrow Br_2 + Br^- \qquad k = 5 \times 10^9\ M^{-1}\ s^{-1}\ \text{(assumed)}$$

$$2Br^\bullet \rightarrow Br_2 \qquad k = 5 \times 10^9\ M^{-1}\ s^{-1}\ \text{(assumed)}$$

In this system, the Br^- concentration is ca. 7 × 10^{-7} M according to equilibrium[24] 4.

$$Br_2 + H_2O \rightleftharpoons H^+ + Br^- + HOBr \qquad K_4 = 5 \times 10^{-9}\ M \tag{4}$$

This concentration falls short of giving quantitative agreement between observed and simulated traces.

Additional Br^- formation has to be postulated, presumably in the reaction sequence shown below, initiated by the $^\bullet CH_2OH$ radical:

$$^\bullet CH_2OH + Br_2 \rightarrow BrCH_2OH + Br^\bullet$$

$$BrCH_2OH \rightarrow H^+ + Br^- + CH_2O$$

For the simulation to work, the last reaction should have a rate constant $>10^5\ s^{-1}$. Judging by the short lifetime[25] of CCl_3OH ($\approx$1 μs), this requirement is not unreasonable. The nice fit to the experimental curve lends credit to the employed value of k_{-3}. The buildup rate corresponds to $k(H^\bullet + Br_2) \approx 5 \times 10^9\ M^{-1}\ s^{-1}$. In our hands (several independent measurements over the years), the rate constant k_3 was found to be $(1.2 \pm 0.1) \times 10^{10}\ M^{-1}\ s^{-1}$. While k_3 agrees well with literature values,[23] k_{-3} is significantly lower than previously believed $\{(7 \pm 2) \times 10^5\ s^{-1}$, ref 26; $(3.5 \pm 1) \times 10^4\ s^{-1}$, ref 8$\}$. With the value of k_{-3} at hand, the equilibrium constant K_3 is revised to $6 \times 10^5\ M^{-1}$. From this K_3 value and the well-established[27,28] $E^\circ(Br_2^{\bullet -}/2Br^-) = 1.62$ V vs NHE, we calculate $E^\circ(Br^\bullet/Br^-) = 1.96$ V. Our $E^\circ(Br^\bullet/Br^-)$ is in excellent agreement with the one obtained when the equilibrium constant[29] of 9.6 observed for the reaction $Br^\bullet + OH^- \rightleftharpoons Br^- + OH^\bullet$ is combined with $E^\circ(OH^\bullet/OH^-) = 1.90$ V vs NHE.[30-31] The free energy of formation of the bromine atom in water, $\Delta G^\circ_f(Br^\bullet)_{aq}$, is calculated to be 20.42 kcal/mol, while the free energy of its aqueous solvation, $\Delta G^\circ_{g-aq}(Br^\bullet)$, comes out as 0.73 kcal/mol. If, however, 1 M is taken as the standard state of $Br^\bullet$ in both the gas phase and water, we obtain $\Delta G^\circ_{g-aq}(Br^\bullet) = -1.2$ kcal/mol, which reveals that $Br^\bullet$ is somewhat stabilized through hydration.

In order to gain direct access to the rate constant of $I_2^{\bullet -}$ dissociating into $I^\bullet + I^-$, i.e., k_{-5}, 1,2-diiodoethane was pulsed irradiated:

$$I + I^- \rightleftharpoons I_2^- \tag{5}$$

When ICH_2CH_2I was reduced by e^-_{aq} in the presence of 0.1 M *tert*-butyl alcohol and 10^{-3} M N_3^- to scavenge $OH^\bullet$ and $I^\bullet$ radicals, respectively, the amount of $I_2^{\bullet -}$ promptly formed was found to be 47% of e^-_{aq}, a value slightly higher than that for $Br_2^{\bullet -}$. k_{-5} was measured to be $1.2 \times 10^5\ s^{-1}$, which, combined with $k_5 = 1.2 \times 10^{10}\ M^{-1}\ s^{-1}$, yielded $K_5 = 1.0 \times 10^5\ M^{-1}$, this time in excellent agreement with accepted literature values.[32,33]

How then does the prompt formation of the dihalogenide radical anions proceed? The *in-cage* reaction between $Br^\bullet$ and Br^- can be ruled out, as k_2 cannot compete with diffusion. Furthermore, in ref 16, a limiting rate was measured for the formation of $Br_2^{\bullet -}$ at sufficiently high $[Br^-]$, an observation which we have confirmed. Evidently, this argues against $Br_2^{\bullet -}$ being formed in a reaction between Br^- and $BrCH_2CH_2^\bullet$.

The prompt formation of $Br_2^{\bullet -}$ would seem to constitute a parallel channel to reaction 1. It is noteworthy that, even in the gas phase, some $Br_2^{\bullet -}$ is formed in negative ion mass spectra[34] of 1,2-dibromoethane. The higher yield of promptly formed $I_2^{\bullet -}$ as compared to that of promptly formed $Br_2^{\bullet -}$ is in keeping with the dramatic weakening of the C–halogen bond on going from Br to I.

Hydrogen Abstraction Reactions of $Br^\bullet$. In the presence of a monitor substance (A) which undergoes reaction 6 to form the colored species C, the measured rate of formation of C is $k_{obs} = k_0 + k_A[A]$, where k_0 is the rate in the absence of A. A special case is when A is Br^-, in which case eq 3 applies. Upon addition of a second substance, for instance a hydrogen donor (RH), capable of reacting with $Br^\bullet$ (reaction 7), the observed rate constant for formation of C becomes $k_{obs} = k_0 + k_A[A] + k_7[RH]$.

$$Br^\bullet + A \rightarrow C + Br^- \tag{6}$$

$$Br^\bullet + RH \rightleftharpoons R^\bullet + H^+ + Br^- \tag{7}$$

The size of the signal due to C, OD(C), is then $OD(C) = OD(C_0)k_A[A]/(k_A[A] + k_7[RH] + k_0)$, where $OD(C_0)$ is the optical density that would be measured were all $Br^\bullet$ in the system to react with the monitor A.

We have tried out several monitors, e.g., Br^-, promethazine, and 4-iodophenol. None of them is without drawbacks. As for $Br_2^{\bullet -}$, the kinetics of its formation is unaffected by the presence of the promptly formed $Br_2^{\bullet -}$ (see above), but, due to its rapid radical–radical combination, measurements are limited to reactions having $k_7[RH] > 2 \times 10^5\ s^{-1}$. Promethazine reacts with both $Br^\bullet$ ($k_{(Br + prom)} = 7.5 \times 10^9\ M^{-1}\ s^{-1}$) and $Br_2^{\bullet -}$, which will introduce some systematic errors into the calculated rate constant. However, the promethazinium radical cation formed is more stable than $Br_2^{\bullet -}$, making rate determinations feasible for $k_7[RH] > 10^4\ s^{-1}$. Contrary to Br^- and promethazine, 4-iodophenol can be used for measuring both k_{obs} and OD(C) without the complications introduced by the promptly formed $Br_2^{\bullet -}$. Unfortunately, due to relatively low extinction coefficients, the measurements are not very sensitive. For a detailed listing of conditions for each substrate, see the Experimental Section.

The rate constant k_7 can be obtained from a plot of k_{obs} versus [RH]. Figure 2 is an example of such a plot. Table 1 contains rate constants k_7 extracted from such plots. The value for *tert*-butyl alcohol is in complete agreement with the one obtained

---

(24) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355.

(25) Mertens, R.; von Sonntag, C.; Lind, J.; Merényi, G. *Angew. Chem., Int. Ed. Engl.*, in press.

(26) Treinin, A.; Hayon, E. *J. Am. Chem. Soc.* **1975**, *97*, 1716.

(27) Laurence, G. S.; Thornton, A. T. *J. Chem. Soc., Dalton Trans.* **1973**, 1637.

(28) For an extended discussion, see: Stanbury, D. M. In *Advances in Inorganic Chemistry*; Sykes, A. D., Ed.; Academic Press: San Diego, CA, 1989; Vol. 33, pp 81–83.

(29) Kläning, U. K.; Wolff, T. *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 243.

(30) Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1984**, *88*, 3643.

(31) Kläning, U. K.; Sehested, K.; Holcman, J. *J. Phys. Chem.* **1985**, *89*, 760.

(32) Baxendale, J. H.; Bevan, P. L. T.; Stott, D. A. *Trans. Faraday Soc.* **1968**, *64*, 2389.

(33) Schwarz, H. A.; Bielski, B. H. J. *J. Phys. Chem.* **1986**, *90*, 1445.

(34) Madhusudanan, K. P.; Mittal, S.; Durani, S.; Kapil, R. S. *Org. Mass. Spectrom.* **1985**, *20*, 323.

(35) Seetula, J. A.; Gutman, D. *J. Phys. Chem.* **1992**, *96*, 5401.

(36) Dóbé, S.; Otting, M.; Temps, F.; Wagner, H. Gg.; Ziemer, K. *Ber. Bunsenges. Phys. Chem.* **1993**, *97*, 877.

(37) Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1989**, *93*, 409.

(38) Seakins, P. W.; Pilling, M. J.; Niiranen, J.; Gutman, D.; Krasnoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 9847. Assumed to be the same as that for C_2H_6.

(39) Niiranen, J. T.; Gutman, D., Krasnoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 5881.

(40) Calculated from BDE(R–H) (refs 35 and 36) and data in ref 37.

(41) Calculated from data in ref 37 and references therein.

(42) Calculated assuming $S^\circ(RH)_g - S^\circ(R^\bullet)_g$ to be the same as that for ethane (ref 38). In addition, the free energies of solvation of RH and $R^\bullet$ were set equal.

(43) The mean of the measured (Surdhar, P. S.; Mezyk, S. P.; Armstrong, D. A. *J. Phys. Chem.* **1989**, *93*, 3360) and extracted (from ref 37) values.

(44) Calculated according to $^{10}\log(K_7) = \{E^\circ(Br^\bullet/Br^-) - E^\circ(R^\bullet,H^+/RH)\}/0.059$.

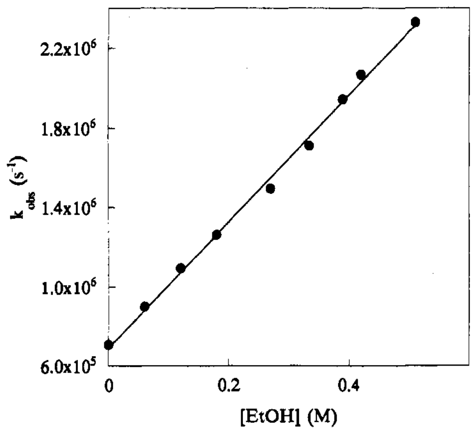

Figure 2. Measured rate constant for the buildup of $Br_2^{\bullet -}$ in the presence of 6×10^{-5} M Br^- and varying amounts of ethanol.

Table 1. Rate and Equilibrium Constants in Water for Reaction 7

RH	k_7 (M^{-1} s^{-1})	BDE-$(R\text{–}H)_g$ (kcal/mol)	$E°(R^\bullet,H^+/RH)_{aq}$ (V) (vs NHE)	K_7[k] (M)
CH_3OH	3×10^5	98.0[a]	1.76[f]	2×10^3
C_2H_5OH	3.1×10^6	96.7[b]	1.70[g]	2×10^4
$(CH_3)_2CHOH$	6.6×10^6	94.4[b]	1.65[g]	3×10^5
$(CH_3)_3COH$	1.4×10^4	101[c]	1.92[h]	7
CH_3CHO	2.5×10^8 [l]	89.3[d]		
HCO_2^-	4.6×10^8		1.51[j]	4×10^7
4-iodophenol	6.2×10^9	87[e]	1.37[e]	1×10^{10}
adipate^{2-}	$<10^4$	≈98		
$CH_2(OH)_2$	1.9×10^6	(96.5)	(1.72)[i]	(2×10^4)
$CH_2(OH)CO_2^-$	4.9×10^7		(1.61)[i]	(1×10^6)
$CH_3CH(OH)CO_2^-$	2.5×10^8		(1.53)[i]	(2×10^7)

[a] References 35 and 36. [b] Reference 37. [c] Reference 38. [d] Reference 39. [e] Reference 22. [f] Reference 40. [g] Reference 41. [h] Reference 42. [i] See text. [j] Reference 43. [k] Reference 44. [l] Obtained after division of the measured rate by 0.4, the mole fraction of unhydrolyzed acetaldehyde.

from a chain reaction between Br_2 and the alcohol presented in ref 10, if the revised K_3 is used. On the other hand, k_7 values derived[9] from measurements based on chain reactions involving *N*-bromosuccinimide would appear to be too low by a factor of ca. 10.

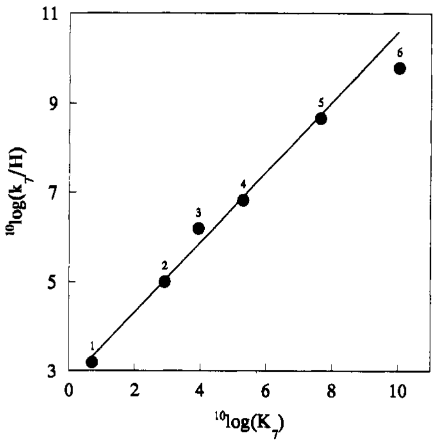

Figure 3. Brønsted plot presenting k_7 per reactive hydrogen atom in RH as a function of the overall equilibrium constant, K_7, of the hydrogen abstraction reaction. (1) *tert*-Butyl alcohol, (2) methanol, (3) ethanol, (4) 2-propanol, (5) formate, and (6) 4-iodophenol.

Table 2. Rate Constant k_7 for the Reaction $Br^\bullet + RH \rightleftharpoons HBr + R^\bullet$ in Different Solvents (k_7 is expressed in M^{-1} s^{-1})

RH	solvent				gas phase
	H_2O[a]	CH_3CN[b]	*t*-BuOH[a]	MeOH[c]	
CH_3OH	3×10^5	9.3×10^5		3×10^5	≈10^4[d]
C_2H_5OH	3.1×10^6	1.6×10^7			
$(CH_3)_2CHOH$	6.6×10^6	4.1×10^7	5.2×10^6		
$(CH_3)_3COH$	1.4×10^4		1.2×10^4		
CH_3CHO	2.5×10^8				2.6×10^9 [e]

[a] This work. [b] Reference 11. [c] Reference 8. [d] Reference 45. [e] Reference 46.

In addition to the rate constants, Table 1 presents a number of other parameters, such as dissociation enthalpies in the gas phase of the reactive C–H (for 4-iodophenol O–H) bond and one-electron reduction potentials at pH 0, i.e., $E°(R^\bullet,H^+/RH)$. Also compiled is K_7, calculated from the latter quantity according to footnote 44. Figure 3 presents a Brønsted plot relating the measured rate constants divided by the number of equivalent hydrogens reacting with $Br^\bullet$ to the equilibrium constants of reaction 7. The bromine atom being selective, it abstracts hydrogens almost invariably from α-C–H bonds, the obvious exceptions being *tert*-butyl alcohol and 4-iodophenol. The plot displays an excellent linearity, yielding the relationship $\log (k_7/H) = 2.53 + 0.81 \log(K_7)$ with a correlation coefficient $r = 0.997$. The value for 4-iodophenol is very close to the estimated diffusion limit and is therefore not expected to lie on the straight line in Figure 3. The good linearity of the plot is evidence that, at least for these substrates, the rate of hydrogen abstraction by $Br^\bullet$ in water probes the free energy of homolysis of the X–H bond being severed, just as the corresponding rate in the gas phase probes the X–H bond strength. From Table 1, the aqueous k_7 rates are also seen to correlate with $BDE(R\text{–}H)_g$ in the gas phase. On the assumption that specific solvation effects are of minor importance, such a trend is not surprising. We note in particular that similar aqueous solvation was suggested[37] for alcohols and their α-hydroxyl radicals, respectively. As can be seen from Table 1, the nice correlation between BDE(C–H) and k_7 breaks down in the case of adipate. In keeping with this finding is the observation[11] that, in acetonitrile, cyclohexane, another 2° hydrogen donor, reacts with $Br^\bullet$ much more slowly than, e.g., methanol. Evidently, heteroatoms accelerate the hydrogen abstraction rate, presumably by way of a polar transition state, to be discussed below in more detail.

The three last entries in Table 1, being alcohols, should conform well to the linear relationship of Figure 3. From the measured k_7 values, K_7 and hence $E°(R^\bullet,H^+/RH)_{aq}$ (presented in parentheses in Table 1) were interpolated. These rate constants reveal that exchanging a methyl group for an OH group in the alcohol leaves the α-C–H bond strength unaffected. On the other hand, interchange of CH_3 with CO_2^- raises the reactivity by a factor of ca. 25, which suggests a weakening of the corresponding α-C–H bond by ca. 2.3 kcal/mol.

There exists a limited number of rate constants, k_7, determined in other solvents. For comparative purposes, these are presented in Table 2. Several conclusions can be drawn from such a comparison. First, it is readily seen that the rate constants measured in water or an alcohol are essentially identical. This is indicative of solvent polarity being of minor importance. The corresponding rates in acetonitrile are even larger than those in water, suggesting that hydrogen-bonding solvents exert a slight retarding influence on k_7. Now, in water, HBr is an extremely strong acid, with a pK_a value somewhere between[47] –5 and –9, depending on the assumed free energy of transfer of *undissociated* HBr from gaseous (1 atm) to aqueous (1 M) standard state. In contrast, HBr in acetonitrile is a weak acid, with $pK_a \approx 5.5$.[48] From this value as well as from data in refs 49 and 50, the Gibbs

---

(45) From ref 35 and Buckley, E.; Whittle, E. *Trans. Faraday Soc.* **1962**, *58*, 536.

(46) Nicovich, J. M.; Shackelford, C. J.; Wine, P. H. *J. Photochem. Photobiol. A* **1990**, *51*, 141.

(47) *Gmelin Handbook of Inorganic and Organometallic Chemistry*, 8th ed.; Br. Supplement Volume B1; Springer-Verlag: Berlin, 1990; pp 385–387 and references therein.

(48) Kolthoff, I. M.; Bruckenstein, S.; Chantooni, M. K., Jr. *J. Am. Chem. Soc.* **1961**, *83*, 3927.

(49) Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Phys. Chem.* **1974**, *76*, 2024.

free energy of formation of HBr in acetonitrile is calculated to be −13.7 kcal/mol (cf. $\Delta G^\circ_f(\mathrm{HBr})_g = -12.77$ kcal/mol and $\Delta G^\circ_f(\mathrm{HBr})_{aq} \equiv \Delta G^\circ_f(\mathrm{Br}^-)_{aq} = -24.85$ kcal/mol).[50] This implies that HBr is solvated more strongly by ca. 11 kcal/mol in water as compared with acetonitrile, a difference almost entirely due to the ionization of HBr in water. As, in spite of this, the corresponding rates, k_7, are somewhat *larger* in CH_3CN, we conclude that ionic dissociation of HBr in water does not influence the transition state of reaction 7. The rate-determining step in the aqueous bromine abstraction reaction probably involves formation of neutral HBr. That the driving force of reaction 7 in water is formation of undissociated HBr rather than $H^+ + Br^-$ is further supported by the slope of the Brønsted plot (Figure 3) being close to 1, which is characteristic of endergonic processes. This suggests the rate-determining step in reaction 7 also to be endergonic, which, however, would seem to be in apparent contradiction with the formal K_7 values all being higher than 1. Nevertheless, if we utilize a pK_a(HBr)[51] between −7 and −8, the formal equilibrium constants, K_7 in Table 1, will be multiplied by a factor of ca. 3×10^{-8}, the elementary steps thus becoming endergonic (with the exception of 4-iodophenol).

As can be seen from Table 2, $Br^\bullet$ reacts very rapidly with CH_3CHO (and also with HCHO)[52] in the gas phase, while this rate is significantly lower in H_2O. This finding probably reflects a specific solvation (presumably hydrogen bonding) of the CHO group by water. If solvated and unsolvated aldehyde are assumed to be in dynamic equilibrium, where only the unsolvated species reacts sufficiently fast with $Br^\bullet$, the apparent low k_7 in water can be appreciated. In one aspect, MeOH behaves curiously. It is seen to react with $Br^\bullet$ more slowly in the gas phase than in either CH_3CN or protic solvents. We note, however, that the reported (and extrapolated to room temperature)[45] gaseous rate constant is not unchallenged.[53]

Reflections on the Mechanism of Hydrogen Atom Abstraction by the Bromine Atom. The present work reveals two sets of observations, the first of them striking. (1) The rate of k_7 for the same substrate is essentially independent of the polarity of the solvent. (2) At similar thermochemistry, k_7 is significantly higher for alcohols than for alkanes.

On the face of it, both of the above observations could be interpreted in terms of a polar transition state coupled with the assumption of the solvent not having sufficient time to adapt to the polarization of the transition state. Finding 1 is in line with the observation that hydrogen abstraction by the cumuloxyl radical is solvent-independent.[54] The hydrogen atom being the lightest nucleus, one certainly would expect the species during hydrogen atom transfer to traverse the transition region more rapidly than in any other type of group-transfer reaction. In support of the above, we recall that recent research[55] has disclosed reaction types where the solvent is not in equilibrium with the reactants in the transition region. While the transition state appears unaffected by the solvent, the latter can affect the reactants by, e.g., specific solvation of the $Br^\bullet$ atom. This is probably the reason for the slightly higher rates in acetonitrile as compared to those in water and alcohols. Similar reasons for solvent influence have been suggested for the reaction of chlorine atoms.[2]

Before addressing point 2, we note that, in the gas phase, the preexponential factors of alcohols reacting with $Br^\bullet$ are lower by a factor of ca. 30 than those for alkanes.[56] This suggests a tighter transition state for alcohols and points to a difference in the nature of the reactions. As for the possible reasons for this difference, we observe that the polar transition state can be pictured as deriving from the in-mixing of charge-transfer states[2,57] **2** and **3** into the major nonpolar component **1** of the transition state:

$$\begin{array}{ccc} R^{\bullet}\dot{H}^{\bullet}Br & R^{+}\dot{H}{:}Br^{-} & {}^{\bullet}RH^{+}{:}Br^{-} \\ \mathbf{1} & \mathbf{2} & \mathbf{3} \end{array}$$

Given that the transition state is a late one, i.e., R–H bond breakage has progressed relatively far, state **2** should be the predominant charge-transfer component. Then, in the sense of simple perturbation theory, the energy of the transition state should be lower the lower the ionization potential of the *radical*, R. Data from ref 58 clearly reveal that α-alkoxyl (and thus probably α-hydroxyl as well) radicals have significantly lower ionization potentials than even alkyl radicals deriving from 3° alkanes. While not for all entries in Table 1 are there ionization potential data of $R^\bullet$ available, we believe the unusually high k_7 value of *tert*-butyl alcohol (where the OH group is β to the primary C–H bonds) to be due to a relatively low ionization potential of the $^\bullet CH_2C(OH)(CH_3)_2$ radical. At any rate, the k_7 values relate poorly to the ionization potentials of the *parent* RH, indicating that charge-transfer state **3** is not a good descriptor of a polar transition state.

The possible rationale of the rate-enhancing effect of a heteroatom being due to an adduct between its lone pair and $Br^\bullet$ is unlikely on the following ground. $Br^\bullet$ forms an adduct to dimethyl sulfide (DMS) stable enough for spectral identification.[59] Furthermore, the C–H bond in DMS[60] is even weaker than that in methanol. These observations suggest that, rather than accelerating the hydrogen atom transfer, adduct formation to the heteroatom in fact inhibits it. Consequently, there is no reason to assume other than a one-step metathesis for reaction 7.

Acknowledgment. We thank the Swedish Natural Science Research Council for its financial support.

---

(50) Atkins, P. W. *Physical Chemistry*, 4th ed.; Oxford University Press: Oxford, 1990; p 941.

(51) As the rate constant of the reverse reaction, $k(R^\bullet + HBr)$, cannot exceed the diffusion-controlled limit, i.e., ca. 10^{10} M^{-1} s^{-1}, the values in Table 1 would seem to demand $-7 < pK_a(\mathrm{HBr}) < -8$.

(52) Nava, D. F.; Michael, J. V.; Stief, L. J. *J. Phys. Chem.* **1981**, *85*, 1896.

(53) Ruscic, B.; Berkowitz, J. *J. Phys. Chem.* **1993**, *97*, 11451.

(54) Avila, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466.

(55) Gertner, B. J.; Wilson, K. R.; Zichi, D. A.; Lee, S.; Hynes, J. T. *Faraday Discuss. Chem. Soc.* **1988**, *85*, 297.

(56) O'Neal, H. E.; Benson, S. W. In *Free Radicals, Volume 2*; Kochi, J. K., Ed.; John Wiley: New York, 1973; p 288 and references therein.

(57) Pross, A.; Yamataka, H.; Nagase, S. *J. Phys. Org. Chem.* **1991**, *4*, 135.

(58) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

(59) Bonifacic, M.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1979.

(60) Stickel, R. E.; Nicovich, J. M.; Wang, S.; Zhao, Z.; Wine, P. H. *J. Phys. Chem.* **1992**, *96*, 9875.