Reaction of a Stable N .˙. N Bonded Radical Cation with Free Radicals generated by Pulse Radiolysis: Exceedingly Rapid Hydrogen Abstraction from C–H Bonds

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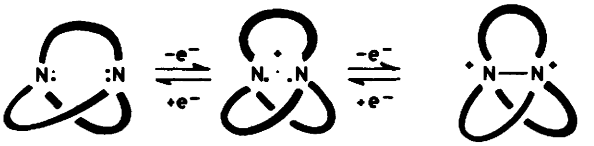
Absolute rate constants have been measured for the reaction of the N .˙. N three-electron bonded 1,6-diazabicyclo[4.4.4]dodecane radical cation ([4.4.4]$^{+\cdot}$) with various free radicals produced by means of pulse radiolysis. Reduction and oxidation reactions occur with rate constants generally somewhat below the diffusion limit. This is considered to reflect the inwardly oriented structure of the [4.4.4]$^{+\cdot}$. High rate constants (*ca.* 10^9 mol^{-1} dm^3 s^{-1}) have been measured for hydrogen-atom abstraction from [4.4.4]$^{+\cdot}$ by almost all radicals except e_{aq}^-. The most remarkable of these reactions appears to be H-atom abstraction by a thiyl radical [$(CH_3)_3CS^\cdot$], which occurs with *k* 3.2 × 10^9 mol^{-1} dm^3 s^{-1}. This indicates highly labile C–H bonds in [4.4.4]$^{+\cdot}$, which are considered to be those located on CH_2 groups α to the nitrogen atoms. The fast radical–radical H-atom transfer is considered to be energetically assisted by favourable stereoelectronics and least heavy atom motion.

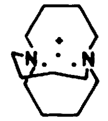
Nitrogen–nitrogen three-electron bonded radical cations (II) are known to exist in one-electron transfer equilibria with diazabicyclo[*k.l.m*]alkanes (I) and the corresponding hydrazonium dications (III).[1–3] Radical cations (II) of high stability are obtained from compounds containing three to five carbon atoms in the intrabridgehead chains. Cyclic voltammetry measurements conducted in CH_3CN solutions have shown that the type (II) species [3.3.3]$^{+\cdot}$, [4.3.3]$^{+\cdot}$, [4.4.3]$^{+\cdot}$, [4.4.4]$^{+\cdot}$, [5.3.3]$^{+\cdot}$, [5.4.3]$^{+\cdot}$, and [6.3.3]$^{+\cdot}$ have lifetimes ⩾0.1 s at room temperature.[4] In all these radical cations the two nitrogen atoms can approach each other without significant strain.[5] Furthermore their geometric structures are most favourable for a nitrogen–nitrogen orbital overlap which is necessary for the formation of the three-electron bond in (II). These three-electron bonds are characterized by two bonding σ-electrons and one antibonding (*i.e.* bond weakening) σ*-electron as described also for a large number of (S .˙. S)$^+$-type radical cations observed in the oxidation of organic sulphides.[6–8] The formation of various nitrogen-centred radical cations (II) *via* reduction of the corresponding hydrazonium dications (III) has been investigated recently by means of pulse radiolysis. Absolute rate constants in the range (1.5—5.0) × 10^{10} mol^{-1} dm^3 s^{-1} were found to be typical for the reactions of various species (III) with hydrated electrons, for example.[9]



(1)

(I) (II) (III)

The most stable cation of this type is [4.4.4]$^{+\cdot}$, with a solid-state structure established by *X*-ray diffraction[10] and a lifetime of months in aqueous solution. It can easily be prepared as a tetrafluoroborate salt, for example, and is stable enough in solution for investigations. The one-electron redox potentials of the [4.4.4] diamine were determined as −0.03 and +0.2(6) V



[4.4.4]$^{+\cdot}$

(*vs.* s.c.e.) for the corresponding (I)/(II) and (II)/(III) couples, respectively, with the second wave only poorly defined, however, because of slow electron transfer.[2,4] These potentials suggest that the [4.4.4]$^{+\cdot}$ radical cation may undergo oxidation as well as reduction reactions. We have previously remarked on the possibility that hydrogen-atom abstraction from [4.4.4]$^{+\cdot}$ by $\dot{C}H_2(CH_3)_2COH$ radicals is extremely fast.[9] We are now able to confirm this suggestion by measurement of absolute rate constants for this and many more examples. For these studies we used pulse radiolysis, which allows the *in situ* generation of the radical reaction partners of [4.4.4]$^{+\cdot}$.

Experimental

The [4.4.4]$^{+\cdot}$ radical cation was prepared as a tetrafluoroborate salt by mixing a solution of 1,6-diazoniatricyclo[4.4.4.0]-tetradecane bistetrafluoroborate[11] (0.300 g) in dry acetonitrile (25 ml) with a solution of 1,6-diazabicyclo[4.4.4]tetradecane[11] (0.159 g) in dry acetonitrile (80 ml), which produced a deep ruby red colour. After 2 h, the solvent was evaporated off under reduced pressure at room temperature to leave the radical cation salt as an almost black crystalline solid. The highest purity was achieved by recrystallization from warm dilute aqueous tetrafluoroboric acid or from ethanol containing aqueous tetrafluoroboric acid. The purity was monitored by measuring the absorbance of [4.4.4]$^{+\cdot}$, which exhibits a broad band with $\lambda_{max.}$ 480 nm and ε 4 600 mol^{-1} dm^3 cm^{-1}. The [4.4.4]$^{+\cdot}$ BF_4^- formed small very dark pinnate *crystals*, decomposing to colourless crystals at 130—132 °C (Found: C, 50.2; H, 8.4; N, 9.6. $C_{12}H_{24}BF_4N_2$ requires C, 50.9; H, 8.5; N, 9.9%); $\nu_{max.}$ (Nujol) 1 340m, 1 180m, 1 050s (B–F), 955m, 900m, and 800m cm^{-1}.

All other chemicals used were of the purest grade commercially available and were employed without further treatment.

The solvent was deionized Millipore-filtered water, the

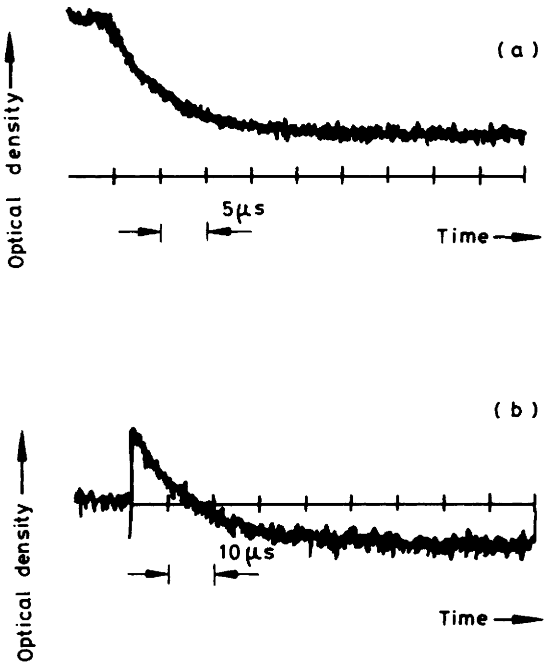


Figure 1. Optical absorption *vs.* time traces monitored at 480 nm in pulse-irradiated, N_2O-saturated, pH *ca.* 4 solutions containing (a) $[4.4.4]^{+\cdot}$ (2×10^{-5} mol dm^{-3}); (b) $[4.4.4]^{+\cdot}$ (2×10^{-3} mol dm^{-3}) and KSCN (10^{-1} mol dm^{-3})

quality of which corresponded to triply distilled water. The solutions were generally prepared either by dissolving the solute directly or by mixing with an appropriate amount of a concentrated stock solution. In order to eliminate oxygen from the solutions nitrogen was generally bubbled through for *ca.* 1 h per 1 dm^3 of solution.

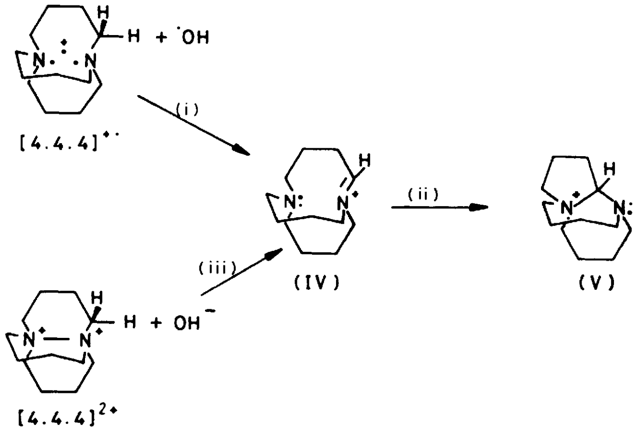
Irradiation of aqueous solutions leads to approximately equal amounts of hydrated electrons (e_{aq}^-) and hydroxyl radicals ($^{\cdot}OH$). If reactions were to be initiated by $^{\cdot}OH$ radicals, the solutions were saturated with N_2O after the deoxygenation. Under these conditions all hydrated electrons were also converted into hydroxyl radicals ($e_{aq}^- + N_2O + H_2O \longrightarrow N_2 + OH^- + {}^{\cdot}OH$).

Pulse radiolysis experiments were performed by exposing the solutions to short pulses of high-energy electrons from a 1.55 or a 3.8 MeV Van de Graaff accelerator. Typical pulse durations were 0.5—5 µs and 5—50 ns for the two machines, respectively. Dosimetry was based on the $^{\cdot}OH$-radical-induced oxidation of thiocyanate to $(SCN)_2^{-\cdot}$. Absorbed doses per pulse were generally in the range 1—10 Gy (1 Gy = 1 J kg^{-1} = 100 rad). This corresponded to an $^{\cdot}OH$ radical concentration of *ca.* (0.6—6) $\times 10^{-6}$ mol dm^{-3} generated per pulse in the N_2O-saturated solutions. Further details on the basic radiation chemistry of aqueous solutions, the pulse radiolysis equipment, and the evaluation of data from experimental absorption–time curves have been given previously.[12]

The experimental limits of error are estimated to be ±10%, unless otherwise noted. All investigations were carried out at room temperature.

Results and Discussion

(1) *Reaction with $^{\cdot}OH$ Radicals*.—The reaction of $[4.4.4]^{+\cdot}$ with $^{\cdot}OH$ radicals was monitored *via* the bleaching of the radical cation absorption and conductivity measurements in pulse-irradiated, N_2O-saturated, pH *ca.* 4 solutions 10^{-5}—10^{-4} mol dm^{-3} in $[4.4.4]^{+\cdot}$. A typical absorption–time trace monitored at 480 nm for a 2×10^{-5} mol dm^{-3} solution is shown in Figure 1(a). Generally the bleaching was found to occur exponentially, with $t_{\frac{1}{2}}$ inversely proportional to the $[4.4.4]^{+\cdot}$ concentration. From this a bimolecular rate constant of $(8.0 \pm 1.0) \times 10^9$ mol^{-1} dm^3 s^{-1} was evaluated. Simultaneous conductivity measurements did not show any change in conductance during the optical bleaching, indicating that the $^{\cdot}OH$ reaction with $[4.4.4]^{+\cdot}$ cannot be a one-electron oxidation process, *i.e.* (2). With neutralization of the OH^- by H_{aq}^+ in the



Scheme.

$$[4.4.4]^{+\cdot} + {}^{\cdot}OH \longrightarrow [4.4.4]^{2+} + OH^- \quad (2)$$

pH 4 solution this reaction would lead to a net negative change in conductivity.[13] This result is certainly remarkable in view of the high oxidation potential of the $^{\cdot}OH$ radical (+1.9 V for $^{\cdot}OH/OH^-$ and +2.7 V for $^{\cdot}OH$, H^+/H_2O).[14]

The experimental results are, however, fully compatible with a hydrogen-atom abstraction, which is also a typical reaction of the $^{\cdot}OH$ radical. A plausible reaction sequence is reaction (i), then (ii), in the Scheme. The small chemical yields from irradiated dilute $[4.4.4]^{+\cdot}$ solutions did not permit product identification, but it is highly likely that the product is the 1-azonia-6-azatricyclo[4.4.4.0^{1,5}]tetradecane ion (V). This is also the product of reaction of the $[4.4.4]^{2+}$ dication with OH^- [reactions (iii) and (ii) in the Scheme].[15] One obvious alternative to reactions (i) and (ii) is electron transfer to give the dication and OH^-, followed by (iii) and (ii). Although accurate kinetics for reaction (iii) are not available, it is certain that this step is far too slow for the $^{\cdot}OH$ reaction to proceed this way,[15] unless special ion-pair cage effects are postulated. As discussed later, hydrogen-atom transfer is indeed the predominant pathway for the reaction of most radicals with $[4.4.4]^{+\cdot}$

A further argument can be advanced, based on the Principle of Least Motion.[16] Reaction (i) in the Scheme involves very little motion of the heavy atoms in the cage molecule. In fact the heavy-atom motion is appreciably less than for the electron-transfer processes $[4.4.4]^{+\cdot} \longrightarrow [4.4.4]^{2+}$ or $[4.4.4]^{+\cdot} \longrightarrow [4.4.4]$, and very much less than for the deprotonation reaction (iii) in the Scheme. Estimates of the extent of heavy-atom motion can be made in the following way. The *X*-ray crystal structures of [4.4.4],[17] $[4.4.4]^{+\cdot}$,[10] and $[4.4.4]^{2+}$ [10] and of the 1-azonia-6-azatricyclo[4.4.4.0^{1,5}]tetradecane ion[18] [(V) in the Scheme] are known. The intermediate 6-aza-1-azoniabicyclo[4.4.4]tetradec-1-ene ion [(IV) in the Scheme] can be modelled as the corresponding alkene (C for N^+), 1-azabicyclo[4.4.4]tetradec-5-ene,[19] for which a molecular mechanics calculation (MM2) is

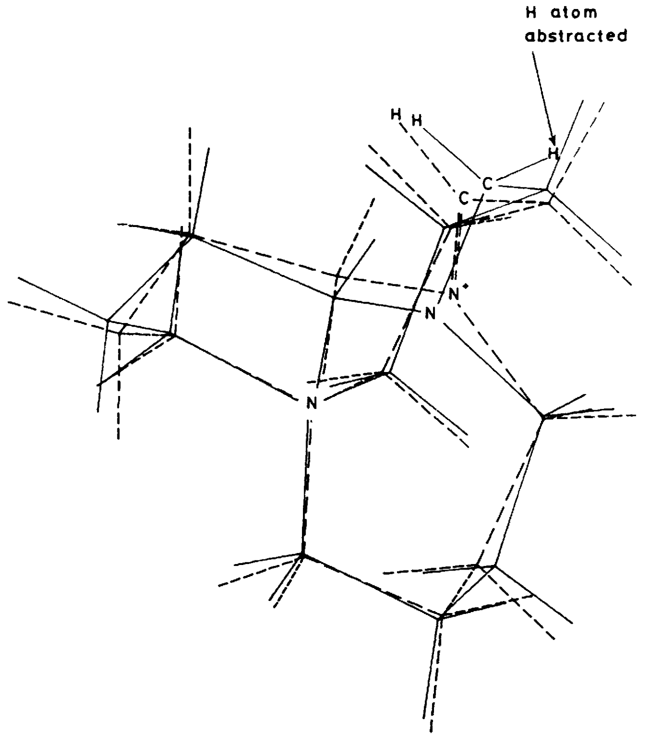


Figure 2. XFIT of $[4.4.4]^{+\bullet}$ (——) and ion (IV) in the Scheme (– – –)

available. The program XFIT[*] superimposes two structures so as to minimize the root mean square of the deviation of corresponding atoms in the two structures. The XFIT of $[4.4.4]^{+\bullet}$ and the ion (IV) is shown in Figure 2; the XFIT r.m.s. deviations, *i.e.* average heavy-atom movements,[†] are:

$$[4.4.4]^{+\bullet} \longrightarrow \text{(IV)}, 0.212; \; [4.4.4]^{+\bullet} \longrightarrow [4.4.4]^{2+}, 0.248;$$
$$[4.4.4]^{+\bullet} \longrightarrow [4.4.4], 0.280; \; [4.4.4]^{2+} \longrightarrow \text{(IV)}, 0.403;$$
$$\text{(IV)} \longrightarrow \text{(V)}, 0.361 \text{ Å}$$

We believe the small amount of heavy-atom movement in $[4.4.4]^{+\bullet} \longrightarrow$ (IV) is a major factor in making hydrogen abstraction from $[4.4.4]^{+\bullet}$ such a favourable reaction pathway. Another, related, factor is the excellent stereoelectronic situation for abstraction of the hydrogen shown in Figure 2 [this equatorial hydrogen (there are six) is undoubtedly the one responsible for the major hyperfine coupling[20] of 49 MHz in the e.s.r. spectrum]. The N–N–C–H torsion angle is 165.7°.

A fast formation of (IV) requires of course that the two electrons forming the C=N double bond (σ^* from three-electron bond and sp^3 after H-atom abstraction) are of opposite spin (no evidence was found for a longer-lived triplet state).

The high rate constant measured for the abstraction reaction suggests that the C–H bond to be cleaved is particularly labile. Depending on whether this refers to both hydrogen atoms in each α-CH_2 group or only one, the rate constant would have to be divided by 12 or 6, respectively, to obtain the reactivity per individual α-C–H bond. In view of the arguments already presented, the latter appears the more likely situation.

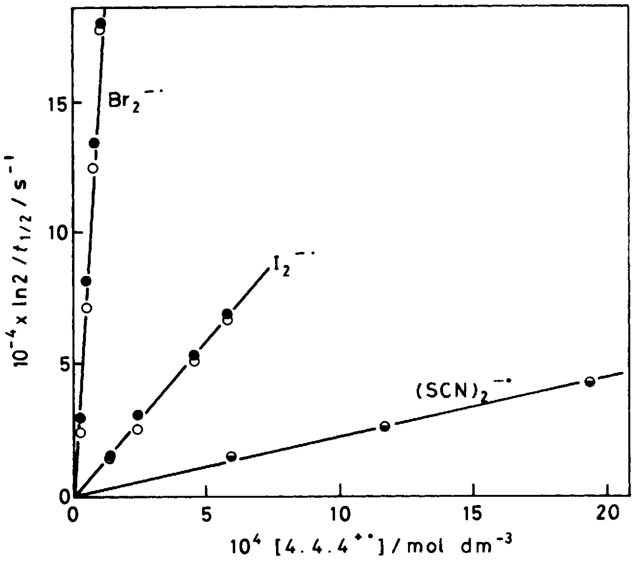


Figure 3. First-order rate constants $k = \ln 2/t_{\frac{1}{2}}$ *vs.* $[4.4.4]^{+\bullet}$ concentration for the reactions of $[4.4.4]^{+\bullet}$ with $Br_2^{-\bullet}$, $I_2^{-\bullet}$ and $(SCN)_2^{-\bullet}$: open symbols, bleaching of $[4.4.4]^{+\bullet}$ at 480 nm; filled symbols, decay of $Br_2^{-\bullet}$ at 360 nm, $I_2^{-\bullet}$ at 380 nm, $(SCN)_2^{-\bullet}$ at 480 nm

(2) *Reactions with* $Br_2^{-\bullet}$, $I_2^{-\bullet}$, *and* $(SCN)_2^{-\bullet}$.—The reactions of $Br_2^{-\bullet}$, $I_2^{-\bullet}$, and $(SCN_2)^{-\bullet}$ radical anions with $[4.4.4]^{+\bullet}$ were investigated in pulse-irradiated, N_2O-saturated solutions containing various small amounts of $[4.4.4]^{+\bullet}$ radical cation [(0.02—2.0) × 10^{-3} mol dm^{-3}], and 10^{-1} mol dm^{-3} of halide or pseudohalide X (Br^-, I^-, or SCN^-; added as potassium salt). Under these conditions the $X_2^{-\bullet}$ radical anions are generated *via* the overall reaction (3) within the duration of even the shortest pulse, and the consecutive reaction of $X_2^{-\bullet}$ with $[4.4.4]^{+\bullet}$ can be monitored by the decay of either or both of the $X_2^{-\bullet}$ and $[4.4.4.]^{+\bullet}$ absorptions. {$Br_2^{-\bullet}$ absorbs with $\lambda_{max.}$ 365 nm, $I_2^{-\bullet}$ with $\lambda_{max.}$ 380 nm, $(SCN)_2^{-\bullet}$ with $\lambda_{max.}$ 475 nm, and $[4.4.4]^{+\bullet}$ with $\lambda_{max.}$ 480 nm; the products $[4.4.4]^{2+}$ and X^- do not exhibit any measurable absorption.} For the reaction of $(SCN)_2^{-\bullet}$ the two processes cannot be separated, since both reactants absorb at about the same wavelength. As can be seen from Figure 1(b) the optical signal (480 nm) first increases, owing to the formation of $(SCN)_2^{-\bullet}$, and then decays to a final value below the base line.

$$2X^- + {}^{\bullet}OH \longrightarrow X_2^{-\bullet} + OH^- \qquad (3)$$

The experimental results of the kinetic analysis are illustrated in Figure 3. It shows a plot of the first-order rate constants, $k = \ln 2/t_{\frac{1}{2}}$, obtained from the exponential decays of the $Br_2^{-\bullet}$, $I_2^{-\bullet}$, and $(SCN)_2^{-\bullet}$ absorptions (filled symbols), and of the bleaching of the $[4.4.4]^{+\bullet}$ absorption (open symbols) as a function of $[4.4.4]^{+\bullet}$ concentration. Straight lines going through the origin are obtained as is expected since the $[4.4.4]^{+\bullet}$ concentration was always much greater than the $X_2^{-\bullet}$ concentration. The bimolecular rate constants for reactions analogous to reaction (2) evaluated from the slopes of the straight lines are 1.7 × 10^9, 1.1 × 10^8, and 2.0 × 10^7 mol^{-1} dm^3 s^{-1} for the reactions of $[4.4.4]^{+\bullet}$ with $Br_2^{-\bullet}$, $I_2^{-\bullet}$, and $(SCN)_2^{-\bullet}$, respectively.

All these rate constants were obtained in solutions containing 10^{-1} mol dm^{-3} of ionic species and therefore are affected by salt effects. This could be corrected by applying $\log k = \log k_0 +$

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[*] XFIT is part of the SHEL-XTL crystallographic program package, running on a Nicolet R3m/E structure analysis system.

[†] Most previous calculations on least motion have been based on computation of the sum of the squares of all atomic displacements (hydrogens included). Mass-weighted displacements have also been used. We have been forced to neglect hydrogen atoms because structures derived from *X*-ray work and calculated by molecular mechanics do not give directly comparable C–H distances. Our procedure is a crude form of mass-weighting.

Table. Rate constants for the reaction of $[4.4.4]^{+\bullet}$ with various radicals.

Transient		k/mol^{-1} dm^3 s^{-1}						
Radical	$E°$/V	Overall	Reduction	%	Oxidation	%	H-Abstraction	%
$^{\bullet}OH$	$+1.9/2.7^{b,14}$	$(8.0 \pm 1.0) \times 10^9$					$(8.0 \pm 1.0) \times 10^9$	100
$Br_2^{-\bullet}$	$+1.7^{21}$	$(2.6 \pm 0.3) \times 10^{9\,a}$			$(9.1 \pm 2.6) \times 10^{8\,a}$	35 ± 10	$(1.7 \pm 0.3) \times 10^{9\,a}$	65 ± 10
$I_2^{-\bullet}$	$+1.0^{21,22}$	$(1.9 \pm 0.2) \times 10^{8\,a}$			$(8.5 \pm 1.9) \times 10^{7\,a}$	45 ± 10	$(1.7 \pm 0.2) \times 10^{8\,a}$	55 ± 10
$(SCN)_2^{-\bullet}$	$+1.33^{23}$	$(4.2 \pm 0.5) \times 10^{7\,a}$			*c*		*c*	
e_{aq}^-	-2.9^{27}	$(1.2 \pm 0.2) \times 10^{10}$	$(1.2 \pm 0.2) \times 10^{10}$	100				
$H^{\bullet}$	-2.3^{27}	$(3 \pm 1) \times 10^9$	*c*				*c*	
$(CH_3)_2\dot{C}OH$	$-1.27^{26\,d}$	$(1.1 \pm 0.2) \times 10^9$	$(4.4 \pm 1.1) \times 10^8$	40 ± 10			$(6.6 \pm 1.1) \times 10^8$	60 ± 10
$CH_3\dot{C}HOH$	$-1.18^{26\,d}$	$(1.3 \pm 0.2) \times 10^9$	$(2.6 \pm 1.3) \times 10^8$	20 ± 10			$(1.0 \pm 0.2) \times 10^9$	80 ± 10
$\dot{C}H_2OH$	$-0.98^{26\,d}$	$(1.5 \pm 0.2) \times 10^9$					$(1.5 \pm 0.2) \times 10^9$	100
$\dot{C}H_2C(CH_3)_2OH$		$(6.8 \pm 1.0) \times 10^8$					$(6.8 \pm 1.0) \times 10^8$	100
$\dot{C}H_3$		$(1.6 \pm 0.2) \times 10^9$					$(1.6 \pm 0.2) \times 10^9$	100
$(CH_3)_3CS^{\bullet}$		$(3.2 \pm 0.3) \times 10^9$					$(3.2 \pm 0.3) \times 10^9$	100

[a] Extrapolated to zero ionic strength. [b] +1.9 V refers to $^{\bullet}OH/OH^-$; +2.7 refers to $^{\bullet}OH, H^+/H_2O$. [c] Not possible to distinguish. [d] Half-wave potentials *vs.* s.c.e.

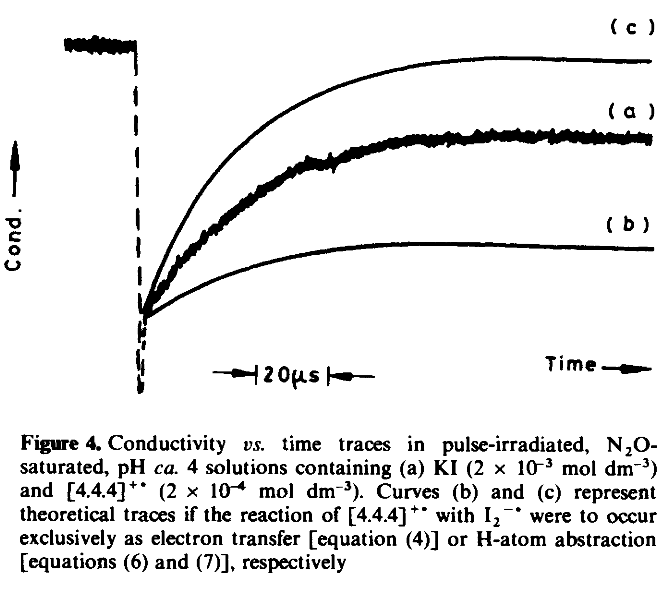

Figure 4. Conductivity *vs.* time traces in pulse-irradiated, N_2O-saturated, pH *ca.* 4 solutions containing (a) KI (2×10^{-3} mol dm^{-3}) and $[4.4.4]^{+\bullet}$ (2×10^{-4} mol dm^{-3}). Curves (b) and (c) represent theoretical traces if the reaction of $[4.4.4]^{+\bullet}$ with $I_2^{-\bullet}$ were to occur exclusively as electron transfer [equation (4)] or H-atom abstraction [equations (6) and (7)], respectively

$1.02 \times z_A \times z_B \times \mu^{\frac{1}{2}}/(1 + \mu^{\frac{1}{2}})$, value k_0 is the rate constant at zero ionic strength, z_A and z_B, the charges on the reacting species, and μ (= 0.1) the ionic strength of the solution. The zero ionic strength rate constants thus derived would be 2.6×10^9, 1.9×10^8, and 4.2×10^7 mol^{-1} dm^3 s^{-1} for the reactions of $Br_2^{-\bullet}$, $I_2^{-\bullet}$, and $(SCN)_2^{-\bullet}$, respectively.

Although the oxidation potentials of $Br_2^{-\bullet}$, $I_2^{-\bullet}$, and $(SCN)_2^{-\bullet}$ are considerably lower (+1.7,[21] +1.0,[21,22] and +1.33 V,[23] respectively) than that of $^{\bullet}OH$, these three radical anions nevertheless usually undergo only one-electron oxidations. The underlying process for the $[4.4.4]^{+\bullet}$ bleaching was therefore suspected to be the general reaction (4) associated with the

$$X_2^{-\bullet} + [4.4.4]^{+\bullet} \longrightarrow 2X^- + [4.4.4]^{2+} \qquad (4)$$

formation of the stable hydrazinium dication. However, reaction (4) seems to account only for part of the overall reaction, as is revealed from simultaneous conductivity measurements. Figure 4(a) shows, for example, a trace of the conductivity signal in a pulsed, N_2O-sat., pH *ca.* 4 solution of I^- (2×10^{-3} mol dm^{-3}) and $[4.4.4]^{+\bullet}$ (2×10^{-4} mol dm^{-3}). The initial decrease of the signal results from reaction (3) plus the immediate neutralization of the OH^- generated therein

$$OH^- + H_{aq}^+ \longrightarrow H_2O \qquad (5)$$

[equation (5)]. Owing to the net loss of one anion ($\Lambda \approx 65\ \Omega^{-1}$ cm^2) and a proton ($\Lambda = 315\ \Omega^{-1}$ cm^2), *i.e.* a total of $\Delta\Lambda \approx -380\ \Omega^{-1}$ cm^2.[13] (Possible differences in specific conductivity between I^- and $I_2^{-\bullet}$ are small and within experimental error limits.) Regeneration of $2I^-$ at the expense of $I_2^{-\bullet}$ and formation of the diammonium $[4.4.4]^{2+}$ at the expense of the singly charged $[4.4.4]^{+\bullet}$ would then lead to an increase in conductivity ($\Delta\Lambda \approx +120\ \Omega^{-1}$ cm^2). This level is indicated by curve (b). The experimental result shows, however, a significantly much greater recovery of the conductivity signal. These results can only be explained if another reaction besides one-electron oxidation is invoked, which by itself would lead to a higher recovery of the conductivity signal. Such a process could be hydrogen abstraction as formulated in principle for the $^{\bullet}OH$ reaction in the previous section, namely (6) followed by (7).

$$X_2^{-\bullet} + [4.4.4]^{+\bullet} \longrightarrow HX + X^- + (IV) \qquad (6)$$

$$HX \longrightarrow H_{aq}^+ + X^- \qquad (7)$$

The associated conductivity change which would lead to full recovery of the signal is displayed as curve (c).*

Analysis of the experimental results on this basis yields electron transfer [reaction (4)] to the extent of *ca.* (35 ± 10)% and (45 ± 10)% for $Br_2^{-\bullet}$ and $I_2^{-\bullet}$ reactions with the remainder to be attributable to the abstraction process. Accordingly, the measured rate constants have to be multiplied by the appropriate percentage to describe the individual oxidation and abstraction processes. The values obtained are listed together with all other kinetic data in the Table. It is interesting that $Br_2^{-\bullet}$ is the most reactive with respect to hydrogen-atom abstraction. This agrees with the fact that HBr has the highest bond strength of all the relevant HX.

For $(SCN)_2^{-\bullet}$ it was not possible to evaluate such data and to distinguish between oxidation and abstraction processes.

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* All signals have been normalized to a quantitative conversion of the primary $^{\bullet}OH + e_{aq}^-$ yield into the final products. Depending on pH the actual yield may be lower due to the $e_{aq}^- + H_{aq}^+ \longrightarrow H^{\bullet}$ reaction.

Figure 5. Conductivity *vs.* time traces in pulse-irradiated deoxygenated (N_2-sat.) solutions of $[4.4.4]^{+\bullet}$ (5×10^{-4} mol dm^{-3}) at pH 3.9; the initial negative spike is of an electronic nature

Owing to the low overall rate constant, concentrations of $[4.4.4]^{+\bullet}$ and SCN^- would have to be chosen which are too high for conductivity experiments.[13] It is assumed though that H-atom abstraction is least efficient for $(SCN)_2^{-\bullet}$ and the reaction is mostly an oxidative electron transfer. In any case it is noted that the rate constants for oxidation are considerably lower than expected for a diffusion-controlled process despite the relatively high oxidation potentials of the $X_2^{-\bullet}$. This was also evident from electrochemical studies on the oxidation of $[4.4.4]^{+\bullet}$.[3] A factor which is likely to slow down electron transfer is a large reorganization energy in going from $[4.4.4]^{+\bullet}$ to $[4.4.4]^{2+}$, as is indicated, for example, by a decrease in N–N distance from *ca.* 2.3 to 1.5 Å in the two species, respectively[10] (see also our discussion on least motion).

Another significant result is that oxidation by $(SCN)_2^{-\bullet}$ is slower than by $I_2^{-\bullet}$, although the latter has the higher oxidation potential. Possibly, removal of an electron (most likely the antibonding σ* electron) from the inwardly oriented structure of $[4.4.4]^{+\bullet}$ requires a certain penetration of the oxidant into the $[4.4.4]^{+\bullet}$ cage, and this would be more hindered in the case of the more bulky $(SCN)_2^{-\bullet}$

Finally, the hydrogen-atom abstractions by $Br_2^{-\bullet}$, $I_2^{-\bullet}$, and possibly $(SCN_2)^{-\bullet}$ substantiate the conclusion derived from the $^\bullet OH$ reaction that α-hydrogen atoms in $[4.4.4]^{+\bullet}$ are particularly labile.

(3) *Reaction with* e_{aq}^-.—A fast reaction of $[4.4.4]^{+\bullet}$ with hydrated electrons is indicated by monitoring the decay of the e_{aq}^- absorption (*e.g.* at 700 nm) in pulsed, N_2-saturated solutions containing varying concentrations of $[4.4.4]^{+\bullet}$ (10^{-5} to 2×10^{-4} mol dm^{-3}). The bimolecular rate constant of $(1.2 \pm 0.2) \times 10^{10}$ mol^{-1} dm^3 s^{-1} derived from these experiments is assigned to the reduction of the radical cation [equation (8)] to

$$[4.4.4]^{+\bullet} + e_{aq}^- \longrightarrow [4.4.4] \qquad (8)$$

yield the diamine. Generation of the latter is, in fact, indicated by an optical absorption which grows in below 300 nm (ε 1 000 mol^{-1} dm^3 cm^{-1} at *ca.* 290 nm and 2 000 mol^{-1} dm^3 cm^{-1} at *ca.* 250 nm) and is characteristic of the diamine.[11] Reaction (8) leads of course to a corresponding bleaching of the radical cation absorption. The overall yield and kinetics of the bleaching also include, however, the $^\bullet$OH-radical-induced process [(i) in the Scheme].

The occurrence of reaction (8) is further supported by conductivity measurements. A corresponding time-resolved trace recorded from pulse-irradiated, N_2-saturated solutions of $[4.4.4]^{+\bullet}$ (5×10^{-4} mol dm^{-3}) at pH 3.9 is shown in Figure 5. At this $[4.4.4]^{+\bullet}$ concentration reaction (8) is almost completed during the *ca.* 1 μs pulse and is seen to be accompanied by an increase in conductivity. Since the $^\bullet$OH reaction [(i) in the Scheme] does not contribute to the signal, the underlying processes are described by the primary ionization of the water [reaction (9)] followed by reaction (8). The net effect from the

$$H_2O \rightsquigarrow H_{aq}^+ + e_{aq}^- + \text{non-ionic species} \qquad (9)$$

conductivity point of view is accordingly the formation of a highly conducting H_{aq}^+ (Λ = 315 Ω^{-1} cm^2 at 18 °C) at the expense of the much less conducting 'normal' cation $[4.4.4]^{+\bullet}$ (estimated Λ ≈ 50 Ω^{-1} cm^2). The absolute yield of the conductivity signal is lower than the initial e_{aq}^- yield and also decreases with decreasing pH. This effect is explained by the competitive reaction of e_{aq}^- with H_{aq}^+ to form $H^\bullet$ atoms and the assumption that the latter do not simply reduce $[4.4.4]^{+\bullet}$ but undergo a different type of reaction [see also section (5)].

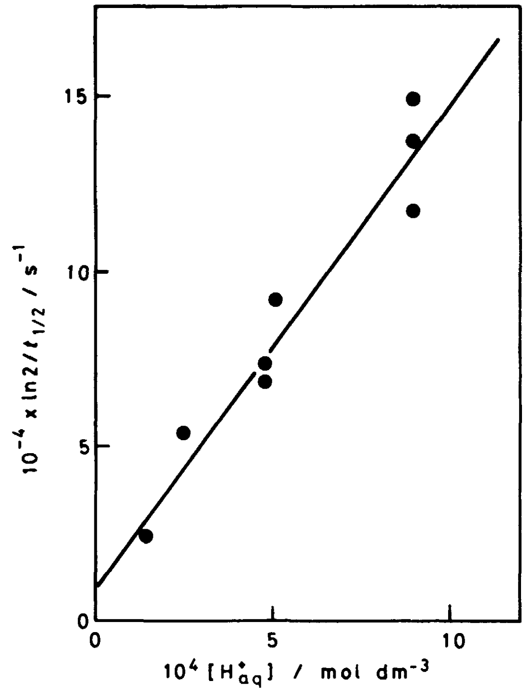
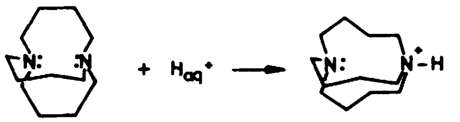


Figure 6. First-order rate constant $k = \ln 2/t_{\frac{1}{2}}$ for the decay of the conductivity signal *vs.* H_{aq}^+ concentration in pulse-irradiated deoxygenated (N_2-sat.) solutions of $[4.4.4]^{+\bullet}$ (5×10^{-4} mol dm^{-3})

At longer times the conductivity signals decrease again to their original (pre-pulse) values. This means that a free proton is re-converted into a normal cation. The measured first-order rate constant of this process linearly increases with the H_{aq}^+ concentration of the solution as is shown in Figure 6. From the slope of the straight line, a bimolecular rate constant of 1.4×10^8 mol^{-1} dm^3 s^{-1} is derived. The most likely underlying reaction which can be envisaged is the protonation of the [4.4.4]-diamine formed in reaction (8), *i.e.* reaction (10),



(10)

leading to the inside-out monoammonium ion (p*K* 6.5). This process requires some energy for the steric rearrangement which is reflected in the relatively low rate constant for the proton addition. The intercept of the straight line in Figure 6 (1×10^4 s^{-1}) would then be attributable to the protonation by water [reaction (11)] occurring with a bimolecular rate constant of about 180 mol^{-1} dm^3 s^{-1} (estimated error limit. factor 2—3).

$$[4.4.4] + H_2O \longrightarrow [4.4.4]H^+ + OH^- \quad (11)$$

A second possibility, namely complete inside protonation of the diamine to yield the extremely stable (VI), cannot occur under our experimental conditions.[24]

(VI)

(4) *Reaction with α-Hydroxyalkyl Radicals.*—α-Hydroxyalkyl radicals are known to be good reductants and were therefore also expected to reduce $[4.4.4]^{+\bullet}$ to the diamine. The possibility of reactions (12)—(14) was investigated in pulse-irradiated, N_2O-

$$(CH_3)_2\dot{C}OH \qquad\qquad (CH_3)_2CO \quad (12)$$

$$CH_3\dot{C}HOH + [4.4.4]^{+\bullet} \longrightarrow [4.4.4] + H^+ + CH_3CHO \quad (13)$$

$$\dot{C}H_2OH \qquad\qquad HCHO \quad (14)$$

saturated pH *ca.* 4 solutions containing $[4.4.4]^{+\bullet}$ [(0.2—1.2) × 10^{-4} mol dm^{-3}] and propan-2-ol, ethanol, or methanol (0.1 mol dm^{-3}). In such solutions the α-hydroxyalkyl radicals are formed *via* H-atom abstraction from the alcohols by $^{\bullet}OH$ radicals.*

The experiments showed fast and exponential bleaching of the $[4.4.4]^{+\bullet}$ absorption by all three radicals, with $t_{\frac{1}{2}}$ inversely proportional to the $[4.4.4]^{+\bullet}$ concentration. From this, second-order rate constants of 1.1 × 10^9, 1.3 × 10^9, and 1.5 × 10^9 mol^{-1} dm^3 s^{-1} were calculated for the three reactions (12), (13), and (14), respectively. The magnitude of these rate constants indicates an almost diffusion-controlled process with little if any activation energy. It is interesting that these rate constants do not follow the reduction half-wave potentials of the a-hydroxyalkyl radicals, according to which the $(CH_3)_2\dot{C}OH$ is the best (−1.27 V) and $\dot{C}H_2OH$ the least efficient (−0.98 V) reductant of the three.[26]

Most interesting additional information on the reaction mechanism is revealed by simultaneous conductivity measurements. Reactions (12)—(14) as formulated would lead to a conductivity signal as described in the previous section for the reduction of $[4.4.4]^{+\bullet}$ by e_{aq}^- (Figure 5) with a yield of $G \times \Delta\Lambda \approx 6 \times 265 \approx 1\,590\ \Omega^{-1}$ cm^2. As can be seen from Figure 7, the experimentally obtained signals for the reactions of $[4.4.4]^{+\bullet}$ with $(CH_3)_2\dot{C}OH$ (a), $CH_3\dot{C}HOH$ (b), and $\dot{C}H_2OH$ (c), respectively, do not reach this limiting value (dashed line). In fact, no change at all in conductivity is obtained for the $\dot{C}H_2OH$ reaction, while the signal heights for the $CH_3\dot{C}HOH$ and $(CH_3)_2\dot{C}OH$ reactions correspond to *ca.* 25% and 45% of the maximum value, respectively. This means that all the $\dot{C}H_2OH$, 75% of the $CH_3\dot{C}HOH$, and 55% of the $(CH_3)_2\dot{C}OH$ reaction must result from a process not accompanied by a change in conductivity. We again suggest this to be a hydrogen-atom abstraction [(15)—(17)], in analogy to reactions (i) in the Scheme and (6). Accordingly, the measured overall rate constants for the $[4.4.4]^{+\bullet}$ bleaching cover both processes. The individual rate constants calculated according to the relative percentages are also listed in the Table. The true rate constants for electron transfer now follow the expected trend. The results also substantiate that hydrogen abstraction is indeed a fast and almost diffusion-controlled process; furthermore the highest rate of abstraction is found for $\dot{C}H_2OH$, *i.e.* for the radical which gains the highest energy upon C–H bond formation.

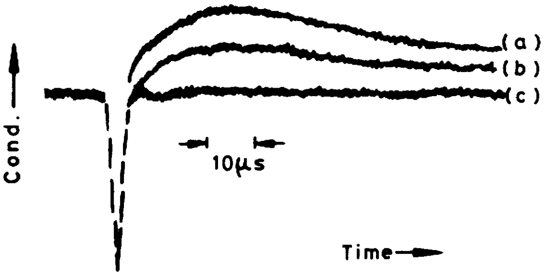


Figure 7. Conductivity signals (normalized) in pulse-irradiated, N_2O-sat., pH *ca.* 4 solutions of $[4.4.4]^{+\bullet}$ (10^{-4} mol dm^{-3}) and either propan-2-ol (a), ethanol (b), or methanol (c) (5 × 10^{-1} mol dm^{-3}). The dashed line represents the theoretical conductivity for quantitative reduction of $[4.4.4]^{+\bullet}$. (The initial negative spike is of an electronic nature)

$$\dot{C}H_2OH \qquad\qquad CH_3OH \quad (15)$$

$$CH_3\dot{C}HOH + [4.4.4]^{+\bullet} \longrightarrow (IV) + CH_3CH_2OH \quad (16)$$

$$(CH_3)_2\dot{C}OH \qquad\qquad (CH_3)_2CHOH \quad (17)$$

(5) *Reaction with Hydrogen Atoms.*—The reaction of hydrogen atoms with $[4.4.4]^{+\bullet}$ could be investigated in very acidic solutions at pH *ca.* 1 where all hydrated electrons generated in the pulse are immediately converted *via* reaction (18). From the

$$e_{aq}^- + H_{aq}^+ \longrightarrow H^{\bullet} \quad (18)$$

kinetics of the $[4.4.4]^{+\bullet}$ bleaching, a bimolecular rate constant of (3 ± 1) × 10^9 mol^{-1} dm^3 s^{-1} was derived. Although the $H^{\bullet}$ atom is also a good reductant ($E^\circ = -2.3$ V[27]) its reaction with $[4.4.4]^{+\bullet}$ may again not be due only to electron transfer [reaction (19)] but also to hydrogen-atom abstraction [reaction

$$H^{\bullet} + [4.4.4]^{+\bullet} \longrightarrow H^+ + [4.4.4] \quad (19)$$

(20)]. Since conductivity measurements are not possible at such

$$H\cdot + [4.4.4]^{+\bullet} \longrightarrow H_2 + (IV) \quad (20)$$

high pH values we could not distinguish between these two reactions in our pulse radiolysis experiments.† The results discussed in section 3 would, however, clearly support the abstraction mechanism [reaction (20)].

(6) *Reaction with Some Other C- and S-Centred Radicals.*—Fast hydrogen-atom abstraction is also observed for the reactions (21)—(23), as is apparent from the bleaching of the $[4.4.4]^{+\bullet}$ absorption and the lack of any conductivity changes in pulse-irradiated, N_2O-saturated, pH *ca.* 4 solutions of various concentrations of $[4.4.4]^{+\bullet}$ (2 × 10^{-5}—10^{-4} mol dm^{-3}) and

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* The reactions of $^{\bullet}OH$ radicals with $(CH_3)_2CHOH$, CH_3CH_2OH, and CH_3OH yield α-hydroxyalkyl radicals with 85.5%, 84.3%, and 93.0% efficiency, respectively.[25]

† The solutions also contained 10^{-1} mol dm^{-3} SCN^- to scavenge the $^{\bullet}OH$ radicals. Since the resulting $(SCN)_2^{-\bullet}$ radical anion reacts only very slowly with $[4.4.4]^{+\bullet}$, positive assignment of the $H^{\bullet}$ atom reaction was possible.

$$\begin{array}{lr}\dot{C}H_3 & CH_4 \quad (21)\\ \dot{C}H_2C(CH_3)_2OH + [4.4.4]^{+\bullet} \longrightarrow & \\ & (IV) + (CH_3)_3COH \quad (22)\\ (CH_3)_3CS^{\bullet} & (CH_3)_3CSH \quad (23)\end{array}$$

5×10^{-1} mol dm^{-3} $(CH_3)_2SO$ [reaction (21)], $(CH_3)_3COH$ [reaction (22)], or $(CH_3)_3CSH$ [reaction (23)]. The underlying processes for transient radical formation are (24)—(26).

$$(CH_3)_2SO + {}^{\bullet}OH \longrightarrow \dot{C}H_3 + CH_3SO_2^- + H^+ \quad (24)^*$$

$$\begin{array}{lcr}(CH_3)_3COH & & \dot{C}H_2(CH_3)_2COH \quad (25)\\ & + {}^{\bullet}OH \longrightarrow H_2O + & \\ (CH_3)_3CSH & & (CH_3)_3CS^{\bullet} \quad (26)\end{array}$$

The rate constant (k_{22}) of 6.8×10^8 mol^{-1} dm^3 s^{-1} found for the $\dot{C}H_2C(CH_3)_2OH$ reaction is somewhat lower (factor 3—4) than a previous estimate of ours, which, however, relied on a more indirect method.[9]

Particularly noteworthy is the high rate constant (k_{21}) of 1.6×10^9 mol^{-1} dm^3 s^{-1} for the $\dot{C}H_3$ radical reaction; maximum rate constants of $\leqslant 10^4$ mol^{-1} dm^3 s^{-1} have generally been found for hydrogen-atom abstractions from C–H bonds by this radical.[30] Even H-atom abstractions from thiols (CH_3 + RSH $\longrightarrow$ CH_4 + $RS^{\bullet}$), which are among the fastest known abstraction reactions by $\dot{C}H_3$, take place only at rates of about 10^8 mol^{-1} dm^3 s^{-1}.[30] This clearly suggests that the α-C–H bond in $[4.4.4]^{+\bullet}$ is weaker than an S–H bond in thiols, and thus substantiates our most remarkable result, namely not only that reaction (23) occurs, but that its rate constant is extremely high (3.2×10^9 mol^{-1} dm^3 s^{-1}). [The same result was obtained incidentally if $(CH_3)_3CS^{\bullet}$ radicals were generated *via* dissociative electron attachment to di-t-butyl disulphide.] Thiols are widely used as hydrogen-atom donors for radical-repair processes (27), particularly in biological systems. A reversible

$$R^{\bullet} + R'SH \longrightarrow R'S^{\bullet} + RH \quad (27)$$

reaction with hydrogen-atom abstraction by thiyl radicals is, however, not completely unknown; it has, for example, been established for the reaction of $RS^{\bullet}$ radicals with HPO_3^-.[31] It seems to us, however, that a direct comparison of these radical–molecule reactions with our present radical–radical processes is not appropriate, particularly since the products of the latter are energetically stabilized diamagnetic molecules. Generally, it is known that free radical centres may labilize adjacent C–H bonds. This is particularly true if the axis of the orbital which carries the unpaired electron is co-planar with the C–H bond. (In this respect it should be noted that the three-electron-bonded system exists in the equilibrium $[N\,\dot{.}\,.\,N]^+ \rightleftharpoons N^{+\bullet} + {:}N$, which requires only *ca.* 60 kJ mol^{-1} to dissociate[9] and thus always provides a singly occupied N-orbital.)

Conclusion

The three-electron-bonded radical cation $[4.4.4]^{+\bullet}$ has been found to react quickly with various types of free radicals. A most significant characteristic of $[4.4.4]^{+\bullet}$ seems to be the pronounced lability of the α-C–H bonds adjacent to nitrogen. Accordingly, hydrogen-atom abstraction is a predominant pathway and successfully competes with one-electron oxidation and reduction processes. Fast H-atom abstraction seems also to be assisted by very favourable stereoelectronics and least heavy-atom motion in the formation of consecutive stable products [reaction (ii) in the Scheme and Figure 2]. The rate constants for the reduction of $[4.4.4]^{+\bullet}$ by some radicals follow the expected trend, but those for the oxidation seem to some extent to reflect the inwardly oriented structure of the $[4.4.4]^{+\bullet}$ radical cation.

Acknowledgements

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* The reaction of ${}^{\bullet}OH$ with $(CH_3)_2SO$ produces a short-lived adduct ($t_{\frac{1}{2}}$ *ca.* 50 ns), which cleaves $\dot{C}H_3$ radicals.[28,29]

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