

The Return of the Succinimidyl Radical

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Dedicated to Professor Lennart Ebersson on the occasion of his 65th birthday

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The aqueous kinetics of the succinimidyl radical, S[•], has been re-examined in the presence of oxidizable substrates and oxygen. The results indicate a rapid equilibrium between S[•] and its ring-opened analogue, the β-(isocyanato-carbonyl)ethyl radical, PI[•]. The equilibrium constant K_1 is ca. 10, with $k_1 \approx 10^7 \text{ s}^{-1}$ and $k_{-1} \approx 10^6 \text{ s}^{-1}$. The glutarimidyl radical, G[•], was produced by one-electron reduction of *N*-chloroglutarimide, GCl. The rate constants of several oxidation and hydrogen abstraction reactions with S[•] and G[•] have been determined. Furthermore, halogen abstraction reactions from haloimides by some selected alkyl radicals were also scrutinised. Most striking is the finding that the 2-cyanoethyl radical abstracts Br from SBr ca. 25 times slower than does the ethyl radical. This demonstrates a strong β-effect and rationalises a relatively slow Br abstraction rate by PI[•] from SBr. While the closure rate of the PI[•] radical appears to be solvent-insensitive, the ring opening rate of S[•], k_1 , is estimated to be ca. 100 times faster in, e.g., CH₂Cl₂ than in water. This suggests hydrogen-bonded stabilisation of S[•].

The present article constitutes part of a collaborative effort between Professor Lennart Ebersson and the first two authors to unravel the elusive mechanisms of imidyl radical chemistry. The results and ideas presented in the paper have been under discussion for a while. Hence it feels appropriate to put them in writing on this occasion.

Ever since the work of Tlumak *et al.*,¹ the succinimidyl radical, S[•], as well as its alkylated analogues have been known to exist in a dynamic equilibrium with their ring-opened isomers.



With S[•] the open species is the β-(isocyanato-carbonyl)ethyl radical, [•]C₂H₄C(O)NCO (PI[•]). In contrast with S[•], the six-membered ring of the glutarimidyl radical, G[•], does not open.² Although there is consensus about the opening of S[•], neither the rate nor the equilibrium constant of S[•]–PI[•] equilibration has been universally established. While Tlumak and coworkers¹ deduce very rapid equilibration in CCl₂H₂ (within nanoseconds or faster), Walling *et al.*³ arrive at slow opening rates (milliseconds) and see no evidence for ring closure. In a previous publication⁴ from our laboratory we have

reported various properties of the succinimidyl radical, S[•], in water. S[•] was produced by means of one-electron reduction of SCl, followed by expulsion of Cl[–]. The rate constant of Cl[–] expulsion to yield S[•] is 10⁶ s^{–1}, which puts an upper limit on the rates that we can measure for reactions involving S[•]. The transient, which we ascribed to S[•], had a relatively long lifetime, disappearing at a rate of ca. 8 × 10⁴ s^{–1}, which we interpreted in terms of ring-opening. Again no indication of ring-closure could be discerned. On the other hand, Kaushal and Roberts⁵ report the rate of ring closure of PI[•], k_{-1} , in cyclohexane to be of the order of 10⁶ s^{–1}. As S[•] is a strong oxidant, it manages rapidly to oxidise a number of substrates and if the colour of the oxidised substrate differs from that of the reduced species, the kinetics of the oxidation can be investigated by optical absorption techniques. Performing such experiments we recently discovered that addition of small amounts of oxygen to the solution resulted in altered kinetics as well as in a decrease in the yield of oxidised substrate. Similar experiments with the glutarimidyl radical, G[•], did not disclose any effect of oxygen. These observations prompted us to reconsider the kinetics of S[•]. At the same time, we report rates of several reactions involving imidyl radicals and hydrogen/electron donors or haloimides and alkyl radicals.

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Experimental

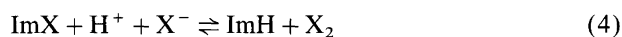
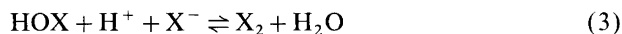
Pulse radiolysis on aqueous solutions was performed at room temperature (22–23 °C), utilising doses of 2–30 Gy/pulse, corresponding to 1.2×10^{-6} – 1.8×10^{-5} M radicals. The 4.6 MeV linear accelerator is characterised by a full width at half maximum of 8 ns and a beam current of 4 A. The computerised optical detection system, which in ideal circumstances (in the absence of overload from Cerenkov radiation, i.e., above ca. 350 nm) has a time resolution of ca. 10 ns, has been described elsewhere.⁶ In all experiments a monochromator bandwidth of 2.5 nm was used. The relative dose/pulse was monitored by the scintillation of an optical fibre placed in front of the cell. The light signal from the fibre was calibrated against an aerated 10^{-2} M KSCN solution taking $G\varepsilon = 2.23 \times 10^4/\text{eV}^{-1} \text{M}^{-1} \text{cm}^{-1}$ at 500 nm.⁷

Chemicals. *N*-Bromosuccinimide (SBr), *N*-chlorosuccinimide (SCl), were purchased from Aldrich while *N*-bromoglutarimide (GBr) and *N*-chloroglutarimide (GCl) were synthesised according to standard procedures. All haloimides were recrystallised from water, vacuum dried and kept in the dark. Solutions of them were prepared immediately before each experiment. The purging gases were purchased from AGA. O₂ and N₂O were of standard preparation, while Ar was 99.99% pure. Tests for any effect of residual oxygen in N₂O were made by comparing the signals from the first and second electron pulse given to the sample. No difference was observed. Except for the haloimides and purging gases all other chemicals (Aldrich or Merck) were used as received.

In order to avoid formation of HOX/X₂ through eqn. (2), equal amounts of the corresponding imide (SH or GH) were added to the haloimide solutions. Abbreviations of chemicals: tris(2,2'-bipyridyl)-ruthenium(II) chloride = Ru(II), 2-methyl-2-propanol = *t*-BuOH.

Results and discussion

Aqueous equilibria. In water the haloimides undergo hydrolysis according to eqn. (2).



In this work we have determined K_4 for GBr by measuring at 286 nm the absorbance of Br₃⁻ formed in eqn. (5). This was achieved by variation of the concentrations of Br⁻, GH, GBr and H⁺.

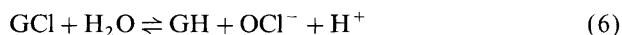


Table 1 contains the measured equilibrium constants. We did not determine any K_2 value for GCl, but by analogy to the SCl system we assume it to be around 10^{-7} .

Table 1. Equilibrium constants for eqns. (2) and (4).

| ImX | K_2 | K_4 | Ref. |
|-----|----------------------|--------------------|-----------|
| GBr | 1.5×10^{-5} | 3×10^3 | This work |
| SBr | 3.5×10^{-6} | 7×10^2 | 10 |
| SCl | 2×10^{-8} | 5×10^{-5} | 17 |

The reduction potential of the glutarimidyl radical, G[·]. The p*K*_a of GH is reported⁸ to be 11.43 and G⁻ appears to undergo rapid hydrolysis. Furthermore, at a pH where enough G⁻ is present to make an experimental determination of the reduction potential $E^\circ(\text{G}^\cdot/\text{G}^-)$ feasible, the starting material GCl is probably hydrolysed to some extent according to eqn. (6).



We estimate K_6 to be close to 10^{-15} , the value for SCl. In spite of these difficulties several attempts were made to establish equilibrium (7).



When GCl was reduced by e_{aq}⁻ at pH values between 10 and 11 in the presence of GH and Cl⁻, Cl₂^{-·} was formed. The yield of Cl₂^{-·} was found to be proportional to [Cl⁻]². A calculated value of $E^\circ(\text{G}^\cdot/\text{G}^-) = 1.90 \text{ V}$ was arrived at. In view of the interference of OCl⁻ this value must be viewed as a generous lower limit. We note in particular that the N–H bond strength of GH estimated⁹ from this E° value and the p*K*_a turns out to be 25 kJ mol⁻¹ lower than that of SH, an inordinately large difference. It is reasonable to assume similar N–H BDEs for GH and SH. With this assumption $E^\circ(\text{G}^\cdot/\text{G}^-) \approx E^\circ(\text{S}^\cdot/\text{S}^-) - 0.12 \text{ V}$ is obtained, i.e., $E^\circ(\text{G}^\cdot/\text{G}^-)$ turns out still lower than $E^\circ(\text{S}^\cdot/\text{S}^-)$.

Rate constants. Table 2 summarises various rate constants involving the glutarimidyl system. The first four entries represent direct optical detection of the hydrated electron or the oxidised substrate. Upon reacting with e_{aq}⁻ GCl rapidly loses a Cl⁻ ion and is transformed into G[·]. In contrast with the SCl case, no GCl^{-·} could be detected, suggesting that the lifetime of the latter should be well below 10^{-6} s. The G[·] radical is seen to oxidise both Ru(II) and Ir(III)Cl₆³⁻ very rapidly. By way of comparison, the oxidation rate of the succinimidyl radical (S[·]), while still fast, is below that of G[·] by ca. one order of magnitude. This difference is emphasised in Fig. 1.

The remaining entries in Table 2 refer to measurements made by competition kinetics, where variation in both size and rate of change of the signal was utilised in the evaluation of the rate constants. An experimental problem in determining rate constants¹⁰ is the chain reaction depicted in Scheme 1. We have managed to avoid chain conditions, except for three systems, where the derived rate constants are only approximate (see Table 2). In the latter cases the estimated error amounts to about a factor of 2, whilst the uncertainty in the remaining values should not exceed 25%.

Table 2. Various rate constants measured in this work.

| Reaction | $k/M^{-1} s^{-1}$ | Monitor | Conditions |
|---------------------------------|----------------------|-------------------|--|
| $e_{(aq)}^- + GCl$ | 1.9×10^{10} | $e_{(aq)}^-$ | Ar, GCl 10^{-5} – 5×10^{-5} |
| $S^\cdot + Ir(III)Cl_6^{3-}$ | 8.6×10^8 | $Ir(IV)Cl_6^{2-}$ | 10^{-3} SCI-SH, Ar, $Ir(III)Cl_6^{3-}$ 1×10^{-5} – 4×10^{-4} |
| $G^\cdot + Ir(III)Cl_6^{3-}$ | 7.6×10^9 | $Ir(IV)Cl_6^{2-}$ | 10^{-3} GCl-GH, Ar, $Ir(III)Cl_6^{3-}$ 1×10^{-5} – 1×10^{-4} |
| $G^\cdot + Ru(II)$ | 1.1×10^{10} | Ru(II) | 2×10^{-4} GCl-GH, Ar, Ru(II) 2×10^{-5} – 2×10^{-4} |
| $G^\cdot + Br^-$ | 2.3×10^9 | $Br_2^{\cdot -}$ | 5×10^{-3} GBr-GH 10^{-2} <i>t</i> -BuOH, N_2O , Br^- 5×10^{-5} – 1.5×10^{-4} |
| $G^\cdot + t\text{-BuOH}$ | 4.1×10^7 | Ru(II) | 4×10^{-5} Ru(II) 10^{-3} GCl-GH Ar, <i>t</i> -BuOH 0 – 10^{-2} |
| $G^\cdot + MeOH$ | $\approx 10^8$ | $Ir(IV)Cl_6^{2-}$ | 2×10^{-4} $Ir(III)Cl_6^{3-}$, N_2O , GCl 10^{-4} – 10^{-2} , MeOH 10^{-2} – 10^{-1} |
| $G^\cdot + ACN$ | 6.4×10^5 | Ru(II) | 90% ACN 10% H_2O , 10^{-2} GCl-GH, Ar, Ru(II) 10^{-4} – 10^{-3} |
| $S^\cdot + ACN$ | 1.2×10^5 | Ru(II) | 90% ACN 10% H_2O , 10^{-2} SCI-SH, Ar, Ru(II) 10^{-4} – 10^{-3} |
| $S^\cdot + ACN$ | 1.2×10^5 | Ru(II) | 10^{-3} SCI-SH, 10^{-4} Ru(II), Ar, ACN 0 – 19 M |
| $S^\cdot + MeOH$ | 1×10^7 | $Br_2^{\cdot -}$ | 0.6 <i>t</i> -BuOH, 10^{-2} SBr, 2×10^{-4} Br^- , N_2O , MeOH 0 – 5×10^{-2} |
| $S^\cdot + C_6H_6$ | 5×10^8 | Ru(II) | 10^{-2} SCI-SH, 2×10^{-2} MeOH, 10^{-4} Ru(II), Ar, C_6H_6 2×10^{-4} – 10^{-3} |
| $(CH_3)_2C(OH)CH_2^\cdot + GBr$ | 3.7×10^8 | $Br_2^{\cdot -}$ | 10^{-2} <i>t</i> -BuOH, 2×10^{-4} , Br^- , N_2O , GBr 2×10^{-4} – 10^{-3} |
| $(CH_3)_2C(OH)CH_2^\cdot + GCl$ | 8.7×10^5 | Ru(II) | 10^{-4} Ru(II), 10^{-2} <i>t</i> -BuOH, N_2O , GCl 5×10^{-3} – 2×10^{-2} |
| $C_2H_5^\cdot + SBr$ | 2×10^9 | Ru(II) | 10^{-4} Ru(II), 2×10^{-2} <i>t</i> -BuOH, 5×10^{-3} C_2H_5Br , Ar, SBr 5×10^{-5} – 1.5×10^{-4} |
| $CNC_2H_4^\cdot + SBr$ | 7.7×10^7 | Ru(II) | 0.1 ClC_2H_4CN , Ar, SBr 10^{-4} – 10^{-3} |
| $\cdot CH_2OH + SCI$ | $\approx 10^9$ | $Ir(IV)Cl_6^{2-}$ | 2×10^{-4} $Ir(III)Cl_6^{3-}$, N_2O , SCI 10^{-4} – 10^{-2} , MeOH 10^{-2} – 10^{-1} |
| $\cdot CH_2OH + GCl$ | $\approx 10^9$ | $Ir(IV)Cl_6^{2-}$ | 2×10^{-4} $Ir(III)Cl_6^{3-}$, N_2O , GCl 10^{-4} – 10^{-2} , MeOH 10^{-2} – 10^{-1} |

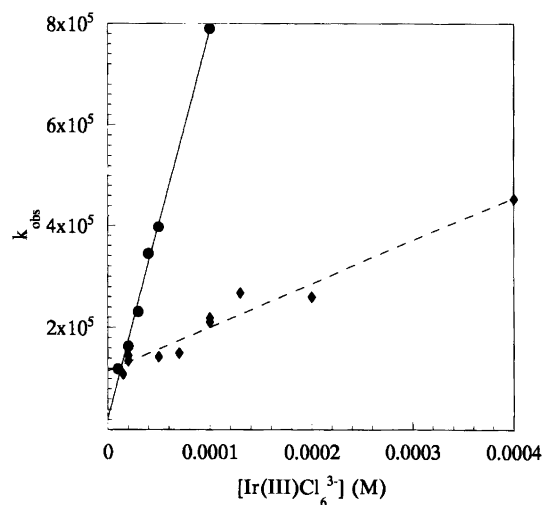
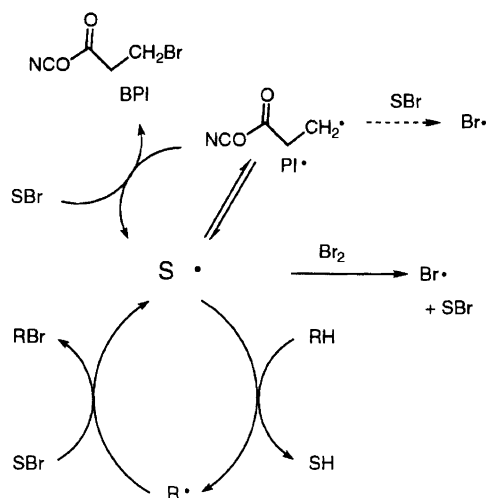


Fig. 1. The observed rate constant of the reaction between S^\cdot (●) or G^\cdot (◆) with $Ir(III)Cl_6^{3-}$. Conditions: argon-purged neutral solutions containing 10^{-3} SCI-SH or GCl-GH.

Halogen abstraction from haloimides by alkyl radicals. The rates of halogen abstraction reactions in Table 2 reveal a number of interesting things.

1. The rate of bromine abstraction is strongly dependent on the nature of the alkyl radical, both steric and polar effects affecting the rate. A finding of particular interest is the very strong β -effect upon going from the ethyl to the 2-cyanoethyl radical. As the $C(O)NCO$ group is even more electron-withdrawing than CN, this suggests that the rate constant of bromine abstraction



Scheme 1.

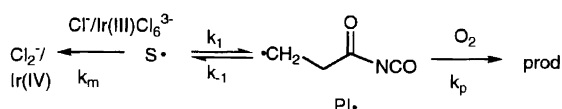
from SBr by the PI^\cdot radical is even lower than $7 \times 10^7 M^{-1} s^{-1}$.

2. A factor of more than 100 between GBr and GCl is seen. Such a factor was also found between the reported rate constants for halogen abstraction from *N*-bromo-¹¹ and *N*-chloro-3,3-dimethylglutarimide¹² (DMGBr, DMGCl) by the cyclopropylcarbinyl radical (CPC^\cdot); $k(CPC^\cdot + DMGBr) = 1.3 \times 10^{10} M^{-1} s^{-1}$ and $k(CPC^\cdot + DMGCl) = 3.6 \times 10^7 M^{-1} s^{-1}$. These observations quantify the rationale given earlier for the absence of ring-opened products when SCI solutions were photolysed.¹³ Clearly, at usual SCI concentrations Cl

abstraction from SCl by $\cdot\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{NCO}$ is far too slow to compete with the effective disappearance of $\text{S}\cdot$.

3. Comparison of the rate constants of Br abstraction by $\cdot\text{CH}_2(\text{CH}_3)_2\text{COH}$ from GBr (see Table 2) and SBr ($k = 1.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$)¹⁰ suggests that the N–Br bond is slightly weaker in GBr than in SBr. Indeed, as the bromine abstraction reaction is almost thermoneutral,⁴ the logarithm of its rate constant should vary with $1/2\Delta\text{BDE}(\text{N–Br})$, as follows from the generalised Marcus equation.¹⁴ $\Delta\text{BDE}(\text{N–Br})$ is thus predicted to be $2RT \ln 2 = 3.4 \text{ kJ mol}^{-1}$. We note that K_4 , which is a measure of the difference between N–H and N–Br bond strengths is four times higher for GBr than for SBr. On the assumption that only the $\text{BDE}(\text{N–Br})$ s differ while the N–H bond strengths are unaffected, the ratio of the two K_4 values should be 4, which is what we find experimentally. In conclusion it is safe to assume that SH and GH have similar N–H bond strengths.

Rate constants of imidyl radical reactions. The most striking feature of Table 2 is that the rate constants of oxidation are higher with $\text{G}\cdot$ than with $\text{S}\cdot$ by ca. an order of magnitude. This is illustrated in Fig. 1 with $\text{Ir}(\text{III})\text{Cl}_6^{3-}$ as the substrate. Hydrogen abstraction reactions are also an order of magnitude faster for $\text{G}\cdot$ than for $\text{S}\cdot$ (cf. the values in Table 2 and the reported rate constant $k(\text{S}\cdot + t\text{-BuOH}) = (1 \pm 0.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$).⁹ This is hard to understand on thermochemical grounds, as we assumed the N–H bond strengths in SH and GH to be similar and hence the one-electron reduction potential of $\text{S}\cdot$ to be higher than that of $\text{G}\cdot$. Furthermore, the oxidation rates with $\text{G}\cdot$ appear to be diffusion-controlled. Therefore, one would have expected the rate constants with $\text{G}\cdot$ and $\text{S}\cdot$ to be the same to within a factor of 2. Assuming such to be the case we propose the following model. $\text{S}\cdot$ is involved in a rapid opening/closure equilibrium, with $K_1 = [\text{PI}\cdot]/[\text{S}\cdot]$. Only $\text{S}\cdot$ participates in oxidation and hydrogen abstraction reactions on the microsecond timescale. Therefore, this model predicts that K_1 should be ca. 10 within a factor of 2. In this case the rate constants involving $\text{S}\cdot$ are $k = k_{\text{obs}}(1 + K_1)$, where the k_{obs} values are those presented in Table 2. The assumption of rapid equilibrium between $\text{S}\cdot$ and $\text{PI}\cdot$ was substantiated by the following additional experiments, illustrated in Scheme 2. Addition of oxygen or air to a solution containing 10^{-2} M SCl and using Cl^- as a monitor yielded the data in Table 3. As can be seen, addition of air resulted in a decreased yield of oxidised substrate as well as in an increased build-up rate $\text{Cl}_2^{\cdot-}$. Similar experiments were performed with $\text{Ir}(\text{III})\text{Cl}_6^{3-}$. Unfortunately, the OH radical disturbs the kinetic traces as it reacts with $\text{Ir}(\text{III})\text{Cl}_6^{3-}$ to produce $\text{Ir}(\text{IV})\text{Cl}_6^{2-}$ as



Scheme 2.

Table 3. The effect of O_2 on the radiation chemical yield of the $\text{Cl}_2^{\cdot-}$ ion during the reduction of 0.01 M SCl or GCl by e_{aq}^- in the presence of Cl^- .

| Cl^-/M | $G\epsilon^a$ | $k_{\text{obs}}/\text{s}^{-1}$ | Gas | ImCl |
|------------------------|---------------|--------------------------------|-----|------|
| 2.5×10^{-3} | 14 330 | 7.4×10^5 | Ar | SCI |
| 2.5×10^{-3} | 10 270 | 1.1×10^6 | Air | SCI |
| 5×10^{-3} | 19 290 | 1.3×10^6 | Ar | SCI |
| 5×10^{-3} | 13 390 | 1.8×10^6 | Air | SCI |
| 5×10^{-2} | 29 320 | — | Ar | SCI |
| 5×10^{-2} | 25 580 | — | Air | SCI |
| 0.5 | 11 900 | — | Ar | GCI |
| 0.5 | 11 660 | — | Air | GCI |

^a $G\epsilon$ is given in units of $\text{M}^{-1} \text{ cm}^{-1}/(100 \text{ eV})$.

well. The signal from the $\text{OH}\cdot$ radical, which was obtained from N_2O saturated solutions, was then corrected for by subtraction. This procedure introduces some uncertainty, but the overall effect is increased yield of $\text{Ir}(\text{IV})\text{Cl}_6^{2-}$ with increased $[\text{Ir}(\text{III})\text{Cl}_6^{3-}]/[\text{O}_2]$ ratio. Identical experiments on GCl showed that O_2 had no effect on the reactions of $\text{G}\cdot$ with $\text{Ir}(\text{III})\text{Cl}_6^{3-}$. These experiments reveal that imidyl radicals do not react with O_2 , given that the $\text{G}\cdot$ radical does not open. In contrast, the results with $\text{S}\cdot$ confirm a rapid opening/closure, where $\text{PI}\cdot$, being a primary alkyl radical, is expected to react with O_2 to form a peroxy radical, $\text{PIO}_2\cdot$. From the data in Table 3 the rate constant $k(\text{PI}\cdot + \text{O}_2) \approx k_{\text{obs}} = (1.5 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is obtained.

In an attempt to estimate the rate of ring-opening of $\text{S}\cdot$, pulse-radiolysis was performed on Ar-, O_2 - and N_2O -purged solutions containing 10^{-2} M SCl and 10^{-3} M $\text{Ir}(\text{III})\text{Cl}_6^{3-}$. By maximising the oxygen content it was hoped that $\text{PI}\cdot$ would react with O_2 at a rate comparable to k_{-1} . If the rate of equilibration of $\text{S}\cdot$ and $\text{PI}\cdot$ is more rapid than their reactions with $\text{Ir}(\text{III})\text{Cl}_6^{3-}$ and O_2 , the following expression given in eqn. (8) for the yield of $\text{Ir}(\text{IV})$ is obtained,

$$\text{Yield} = k_m[\text{Ir}(\text{III})]/(k_m[\text{Ir}(\text{III})] + k_p[\text{O}_2]K_1) \quad (8)$$

where $k_m = k_{\text{obsm}}(1 + K_1)$ and $k_p = k_{\text{obsp}}(1 + K_1)/K_1$. Note that k_m and k_p are defined in Scheme 2. On insertion of the observed rate constants the yield turns out to be independent of the assumed K_1 , namely, $k_{\text{obsm}}[\text{Ir}(\text{III})]/(k_{\text{obsm}}[\text{Ir}(\text{III})] + k_{\text{obsp}}[\text{O}_2])$. Employing the observed rate constants we calculate the yield of $\text{Ir}(\text{IV})\text{Cl}_6^{2-}$ in O_2 -purged solutions to between 25–40% of the corresponding yield obtained in the absence of O_2 . However, we found that upon saturation of the solution with O_2 , the yield of $\text{Ir}(\text{IV})$ was 60%. This shows that equilibration is not faster than the other reactions. We also note that $\text{PIO}_2\cdot$ reacts extremely slowly, if at all, with $\text{Ir}(\text{III})$, as we see no sign of a slow build-up of $\text{Ir}(\text{IV})$.

At any rate such a reaction is unlikely, given that alkylperoxy radicals have lower reduction potentials¹⁵ ($E^\circ = 0.8 \text{ V}$ vs. NHE) than $\text{Ir}(\text{IV})\text{Cl}_6^{2-}$ ($E^\circ = 1.02 \text{ V}$). As the initially formed radical is $\text{S}\cdot$, the extra yield can

be interpreted in terms of a competition between ring opening of S^{\cdot} and its reaction with Ir(III)Cl_6^{3-} with the rate constant k_m . We assume k_m to be similar to $k(G^{\cdot} + \text{Ir(III)Cl}_6^{3-})$, i.e., $7.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Once PI^{\cdot} is formed two extreme cases are possible: complete equilibration or complete removal of PI^{\cdot} by O_2 . With the assumed k_m the first case will give an upper limit of $1.5 \times 10^7 \text{ s}^{-1}$ to k_1 [20% Ir(IV) is formed in the first turnover], while the latter gives the lower limit of $5 \times 10^6 \text{ s}^{-1}$ (60% yield in direct competition). Clearly, the uncertainty in k_1 is no more than a factor of three, and its order of magnitude is not in doubt. In combination with $K_1 \approx 10$, a closure rate constant k_{-1} of ca. 10^6 s^{-1} is obtained. Kaushal and Roberts⁵ measured the ratio between k_{-1} and the hydrogen abstraction rate of PI^{\cdot} from Et_3GeH . Assuming the latter rate constant to be close to that of the 1-hexenyl radical they estimated k_{-1} in cyclohexane at around room temperature to be ca. $1 \times 10^6 \text{ s}^{-1}$. Thus k_{-1} would seem to be insensitive towards the solvent. Utilising this value of k_{-1} and the selectivity of ring closure vs. Br abstraction of PI^{\cdot} from SBr ,¹ we calculate $k(\text{PI}^{\cdot} + \text{SBr})$ to be ca. $3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, a reasonable value, judging from Table 2. The k_1 value found in this paper is much higher than our previously reported⁴ figure of $8 \times 10^4 \text{ s}^{-1}$, and is seen as the intercept in Fig. 1. As expected for G^{\cdot} , which does not ring-open, no statistically significant intercept is obtained. The latter value refers to a reaction of PI^{\cdot} , presumably hydrolysis. In this context it is noteworthy that a substantial intercept of ca. 10^5 s^{-1} can be seen in Fig. 1 for S^{\cdot} while for G^{\cdot} the intercept is much lower. An equilibrium constant K_1 of ca. 10 will slightly modify the thermodynamic parameters of the succinimidyl system previously reported.⁴ Thus $E^{\circ}(S^{\cdot}/S^{\ominus})$ should be raised to ca. 2.28 V vs. NHE, which results in a corresponding increase of ca. 6 kJ mol^{-1} in the N–H, N–Br and N–Cl bond strengths.

As most experiments on succinimidyl radicals have been done in CH_2Cl_2 , an estimate of K_1 in that solvent should be of interest. As has been shown¹⁶ K_1 in CH_2Cl_2 is ca. 100 times higher than in water, i.e., ca. 10^3 . From

this it follows that k_1 should be around 10^9 s^{-1} in CH_2Cl_2 . The lower k_1 value in water is probably caused by hydrogen-bonded stabilisation of S^{\cdot} .

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