Photoreactions of the decatungstate anion $W_{10}O_{32}{}^{4-}$ with organic substrates in solution studied by EPR and kinetic absorption spectroscopy: an example for the persistent radical effect

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EPR and kinetic absorption spectroscopy experiments reveal the simultaneous formation of transient radicals and a persistent reduced tungsten radical species during the photoreaction of $W_{10}O_{32}{}^{4-}$ with organic substrates in solution. It is shown that a special kinetic effect operates which causes the observed selective product formation. Theoretical predictions on the ratio of radical concentrations and on their time developments are confirmed. Moreover, some mechanistic aspects of the reactions are clarified.

Photochemical reactions of polyoxometalate anions, such as the decatungstate $W_{10}O_{32}{}^{4-}$, in liquid solution can lead to useful transformations of organic substrates, *e.g.*, to the catalytic ethylation, vinylation, carbonylation and hydroperoxidation of alkanes.[1–4] Many details of the mechanism are still unexplored. However, for tetrakis(tetra-*n*-butylammonium)decatungstate in non-acidified acetonitrile the basic reactions are established and, in part, also supported by quantum chemical calculations.[5]

After UV excitation in the longest wavelength band of $W_{10}O_{32}{}^{4-}$ (290–400 nm) a reactive excited state $W_{10}O_{32}{}^{4-}*$ is reached within 30 ps.[1d,3a] This may be a triplet state,[2a] and it reacts with suitable hydrogen donors RH, the solvent and possibly the tetra-*n*-butylammonium cation on the 10–200 ns timescale[1d,2b,3] to a reduced paramagnetic tungsten species and a transient radical $R^{\bullet}$ [reaction (1)]. The former is written here as $H^{+}W_{10}O_{32}{}^{5-}$ but the protonation state is unclear.[1a,3a]

$$W_{10}O_{32}{}^{4-}* + RH \longrightarrow H^{+}W_{10}O_{32}{}^{5-} + R^{\bullet} \qquad (1)$$

In the microsecond time range a reverse hydrogen atom transfer [reaction (2)] converts part of the reduced species and

$$H^{+}W_{10}O_{32}{}^{5-} + R^{\bullet} \longrightarrow W_{10}O_{32}{}^{4-} + RH \qquad (2)$$

the radicals[2b,c] back to the reactants. Simultaneously, the transient radicals undergo normal diffusion controlled coupling and disproportionation.

$$2R^{\bullet} \longrightarrow P \qquad (3)$$

With alkenes, alkynes, carbonmonoxide or oxygen (S) they also react by addition, and the resulting transient adduct radicals $RS^{\bullet}$ yield the ethylation, vinylation, carbonylation and hydroperoxidation products in a reaction analogous to (2) [reaction (4)].

$$H^{+}W_{10}O_{32}{}^{5-} + RS^{\bullet} \longrightarrow W_{10}O_{32}{}^{4-} + RSH \qquad (4)$$

Further, the reduced tungsten species disproportionate on the rather long timescale of milliseconds to seconds[2] [reaction (5)], *i.e.* they are rather persistent. In the presence of heterogeneous catalysts reaction (5) leads to the evolution of molecular hydrogen.[2c]

$$2H^{+}W_{10}O_{32}{}^{5-} \longrightarrow H_2W_{10}O_{32}{}^{4-} + W_{10}O_{32}{}^{4-} \qquad (5)$$

Here, we apply CW-EPR-spectroscopy and time-resolved laser flash photolysis in the µs time range to the photoreaction of the decatungstate anion $W_{10}O_{32}{}^{4-}$ with a variety of organic substrates in acetonitrile. Special emphasis is placed on the direct detection of the paramagnetic intermediates to obtain further insight in the mechanisms and the kinetics.

Moreover, we demonstrate that the reaction provides a clear example for the so-called Persistent Radical Effect. This kinetic effect was first explored several years ago.[6a,b] It explains unusually high yields of radical cross-reactions which are analogous to the dominance of reactions (2) and (4) over reaction (3) in the scheme considered here. Later, the effect was found to operate in a variety of other organic radical reactions[7] and in 'living' radical polymerization.[6c]

In short, the principles of the Persistent Radical Effect are: if transient and persistent radical species are formed continuously with equal rates as in reaction (1) the self-reaction of the transient species, *e.g.* reaction (3), leads to an excess of the persistent radicals building up in time. Hence, the cross-reaction (2) accelerates, and this diminishes the role of reactions (3) and (5) as time evolves, *i.e.* the reaction system shows features of self-regulation. When the transient radicals are converted to other transients as in reaction (4) the cross-reaction of the new radical derivatives with the persistent species becomes the dominant product formation path. Here, $W_{10}O_{32}{}^{4-}$ is regenerated in reactions (2) and (4), and the dominance of these regeneration reactions explains the catalytic behaviour. For a pulse radical formation the kinetics of the transient radicals is unusual and does not follow simple rate laws. This is also dealt with below.

Experimental

Tetrakis(tetra-*n*-butylammonium)decatungstate was prepared as colorless to slightly yellowish crystals following literature prescriptions[8] and was purified by repeated recrystallization from 1 : 1 mixtures of dimethylformamide and either toluene, ethanol or acetone. The absorption spectrum in acetonitrile (onset at $\lambda = 400$ nm, $\lambda_{\max} = 322$ nm, $\varepsilon_{\max} = 14\,500$ M^{-1} s^{-1}) agreed with earlier findings.[1d,2b] All other chemicals were purchased in the purest available forms and used as received.

EPR spectra of the transient and the persistent radicals ($H^{+}W_{10}O_{32}{}^{5-}$) were observed during continuous photolysis ($280 < \lambda/\text{nm} < 340$) of deoxygenated acetonitrile solutions containing 2.4 mM $W_{10}O_{32}{}^{4-}$ and 10 vol% substrate. To avoid side-reactions of products the solutions flowed slowly (0.3 ml min^{-1}) through a thermostatted flat quartz cell of 0.4 mm optical pathlength in the EPR cavity. Relative radical concentrations were determined in the temperature range of −20–20 °C from EPR line amplitudes and widths with proper allowance for the different spectrometer settings. Due to the large linewidths differences they are only approximate and have estimated errors of up to a factor of 5.

The laser flash photolysis apparatus has been described previously.[9] It employs a Lambda Physik LPX 100 excimer laser at 308 nm and a flow system and has a dead time of about 100 ns. Usually, the decatungstate was used in 0.1–0.2 mM concentration and all experiments were carried out at room temperature.

Reaction kinetics

In this section we will comment in short on the peculiar kinetics associated with the Persistent Radical Effect.

CW experiments

For continuous photolysis, the kinetic equations for the concentrations of the transient (R) and the persistent species ($Y = H^+W_{10}O_{32}^{5-}$) are given in eqn. (6), where I denotes the rate

$$\frac{d[R]}{dt} = I - k_x[R][Y] - 2k_{tR}[R]^2 = 0 \tag{6a}$$

$$\frac{d[Y]}{dt} = I - k_x[R][Y] - 2k_{tY}[Y]^2 = 0 \tag{6b}$$

of radical generation in reaction (1), k_x is the rate constant for the cross-reaction between the transient and the persistent species [reaction (2)], and $2k_{tR}$ and $2k_{tY}$ are the rate constants of the self-reactions (3) and (5). Obviously, in the steady-state the concentrations obey eqn. (7).

$$[Y]/[R] = \sqrt{k_{tR}/k_{tY}} \tag{7}$$

The self-reaction of the transient radicals (3) is expected to be diffusion controlled, *i.e.* $2k_{tR} \approx 5 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$. For reaction (5) $2k_{tY} = 6 \times 10^5\ \text{M}^{-1}\ \text{s}^{-1}$ has been reported.[2c] Hence, one should observed the two radicals in a steady-state concentration ratio of about $[Y]/[R] \approx 100$, *i.e.* a large excess of the persistent species as noted above. The ratio of the rates for the cross- and the self-reactions of R and Y [reaction (2) *vs.* (3) and (5)] is given in eqn. (8).

$$k_x[R][Y]/2k_{tR}[R]^2 = k_x[R][Y]/2k_{tY}[Y]^2 = k_x/2\sqrt{k_{tR}k_{tY}} \tag{8}$$

For a close to diffusion-controlled k_x as inferred from data in ref. 2*c* and the other parameters as given above, eqn. (8) shows that the cross-reaction (2) is the dominant product formation pathway, eventually replaced by reaction (4). This causes the high reaction selectivity,[1–4] and is one of the essential features of the Persistent Radical Effect.[6a]

Time resolved experiments after laser pulse radical generation

Earlier laser flash investigations have shown[1d,2b,c,3a] that excited $W_{10}O_{32}^{4-}$ reacts within 100 ns with the solvent or the substrates by hydrogen atom abstraction. Hence, on our timescale of 0.1–50 μs reaction (1) should appear instantaneous. However, reaction (5) does not take place appreciably before about 50 μs after the laser pulse and can be neglected in the μs timescale. The appropriate kinetic equations for the radical concentrations are given by eqn. (9) with the initial

$$\frac{d[R]}{dt} = -k_x[R][Y] - 2k_{tR}[R]^2 \tag{9a}$$

$$\frac{d[Y]}{dt} = -k_x[R][Y] \tag{9b}$$

condition $[R](t = 0) = [Y](t = 0)$. We have not found a closed analytical solution of these equations but it is clear that [R] will decay to zero whereas [Y] reaches a non-zero final value. Only partial decay of $H^+W_{10}O_{32}^{5-}$ has been observed,[2c,3a] but was not explained properly. A previous analysis as a simple second-order process neglected the effect of the self-termination of R on the kinetics of Y and is not appropriate. Below, Fig. 4 gives an experimental example for the general behaviour of the solutions of eqn. (9) together with a numerical fit.

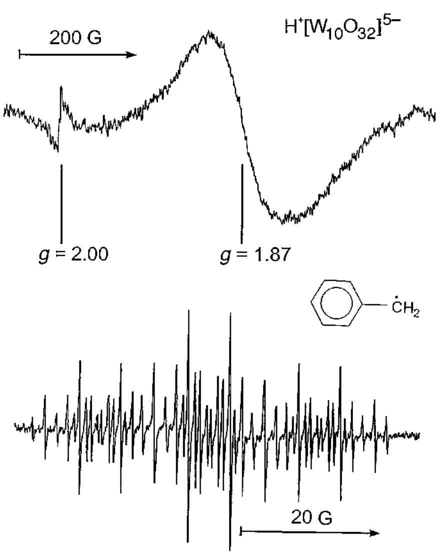

Fig. 1 EPR spectra obtained during the photoreaction of $W_{10}O_{32}^{4-}$ in acetonitrile containing 10 vol% toluene. Upper part: $H^+W_{10}O_{32}^{5-}$; lower part: benzyl radical.

By elimination of the time variable from eqn. (9) one can derive[10] a relation between the concentration of R and Y [eqn. (10)]. At long times when the concentration of R

$$[Y] = [Y](t = 0)\{(1 - [R]/[Y])k_x/2k_{tR} + [R]/[Y]\}^{1/(2k_{tR}/k_x - 1)} \tag{10}$$

approaches zero, that of the persistent species is given by eqn. (11), which is $[Y](t = \infty) = [Y](t = 0)/e$ for $k_x = 2k_{tR}$. Eqn.

$$[Y](t = \infty) = [Y](t = 0)\{k_x/2k_{tR}\}^{1/(2k_{tR}/k_x - 1)} \tag{11}$$

(11) allows a determination of the ratio of rate constants k_x/k_{tR} from the long time limiting concentration of the persistent radical and is used below.

Results and discussion

CW-EPR experiments

Fig. 1 shows EPR spectra obtained during continuous photolysis of the decatungstate in acetonitrile containing 10 vol% toluene at −15 °C. The upper part with the large sweep width reveals a broad strong signal at $g = 1.87$ and a weaker signal at $g = 2.00$. The latter belongs to a carbon centered radical and is distorted by overmodulation and saturation effects. The peak-to-peak width of the broad signal is (125 ± 10) G and decreases upon lowering the temperature as described earlier for the photoreduced decatungstate by Yamase and Usami[2b] and for the electrochemically prepared $W_{10}O_{32}^{5-}$ by Chemseddine *et al.*[8] Hence, it is the tungsten-containing product of reaction (1). The large linewidth precludes the observation of hyperfine splittings and allows for two species with slightly different *g* factors, *e.g.* $H^+W_{10}O_{32}^{5-}$ and $W_{10}O_{32}^{5-}$, as suggested by Jaynes and Hill.[1c] The lower part of Fig. 1 is the spectrum of the carbon centered radical at $g \approx 2.0025$ for higher resolution. The hyperfine pattern is readily assigned to the benzyl radical formed by a hydrogen atom abstraction from the methyl group of toluene. Similar experiments were carried out with a variety of sub-

Table 1 Radicals observed during the photoreaction of $W_{10}O_{32}^{4-}$ in acetonitrile and their relative concentrations

Substrate	Transient radical	$[H^+W_{10}O_{32}^{5-}]$ (10^3 Arbitrary units)	[Y]/[R]
None	Cyanomethyl	5	1600
Toluene	Benzyl	11	160
Ethylbenzyl	1-Phenylethyl	28	370
Diphenylmethane	Diphenylmethyl	20	2000
Cyclopentane	Cyclopentyl	36	900
Methylcyclopentane	1-Methylcyclopentyl	35	2200
Cyclohexene	Cyclohexenyl	10	1400
tert-Butylbenzene	Neophyl	12	4000
Diethyl ether	1-Ethoxyethyl	30	3000
Tetrahydrofuran	2-Tetrahydrofuryl	3	1500
p-Cresol	4-Hydroxybenzyl	7	1800
2,6-Di-*tert*-butyl-*p*-cresol	4-Hydroxy-3,5-di-*tert*-butylbenzyl	18	500
Methanol	Hydroxymethyl	24	12 000
Ethanol	None	23	large
Propan-2-ol	None	21	large
Butan-1-ol	None	9	large

strates. Table 1 gives the observed transient radicals which were identified on the basis of their hyperfine coupling constants, the yields of $H^+W_{10}O_{32}^{5-}$ in arbitrary units and the ratios of the concentrations of the persistent and the transient species [Y]/[R].

Column 3 in Table 1 reveals that the photoreaction (1) occurs with all substrates and with the solvent though with varying efficiency. The nature of the transient radicals (column 2) confirms that abstraction of hydrogen atoms from alkyl groups is the major mechanism. For the cresols the formation of benzyl type radicals is noteworthy since these compounds often lead to the formation of phenoxy species. As is evident from column 3, all alcohols react efficiently with the excited decatungstate, however, the corresponding transient radicals were observed only for methanol. Very probably, this is due to the oxidation [reaction (12)] of the higher α-hydroxyalkyl radicals by the ground state decatungstate ion $W_{10}O_{32}^{4-}$.

$$R\dot{C}HOH \text{ or } R_2\dot{C}OH + W_{10}O_{32}^{4-} \longrightarrow RCHO \text{ or } R_2CO + H^+W_{10}O_{32}^{5-} \quad (12)$$

Since for $W_{10}O_{32}^{4-}$, $E_{red} = -1.2$ V *vs.* Ag/AgNO$_3$,[1c] reaction (12) is very likely for the 2-hydroxy-2-propyl ($E_{ox} = -1.30$ V *vs.* SCE[11]), the 1-hydroxyethyl (−1.18 V *vs.* SCE[11]) and, by analogy, the 1-hydroxy-1-butyl radical, but less so for hydroxymethyl (−0.98 V *vs.* SCE[11]) and the other radicals of Table 1. In an earlier study,[2c] reaction (12) was considered unimportant but we will present additional direct evidence for this reaction below (*cf.* Fig. 5).

Column 4 of Table 1 confirms the predicted large excess of the persistent over the transient species during the continuous photolysis. In view of the errors of the concentration ratios the data grossly agree with the predicted ratio, but also cast some doubt on the value of $2k_{tY}$ used above. Moreover, side-reactions of the transient radicals, *e.g.* reaction (12), may increase the observed values.

In general, the results of this section confirm the mechanism outlined in the introduction. With respect to earlier literature they allow the following additional comments. The formation of the transient hydroxymethyl radical from methanol has also been observed by direct EPR spectroscopy by Yamase and Ohtaka.[2a] Maldotti *et al.*[4c] similarly reported the detection of a transient radical from cyclohexylamine by spin-trapping, and our experiments now confirm that transient radicals are generally involved. It has been suggested that the hydroxyl radical may be the primary product of the photoreaction[4c,12] and act as hydrogen abstraction agent but we find no evidence for this. Further, the quite normal coupling constants of the transient radicals do not support the notion that they remain bound to the polymetalate anion,[5a] and we have also not found any indication for a necessary complexing of the substrates before radical formation.[13]

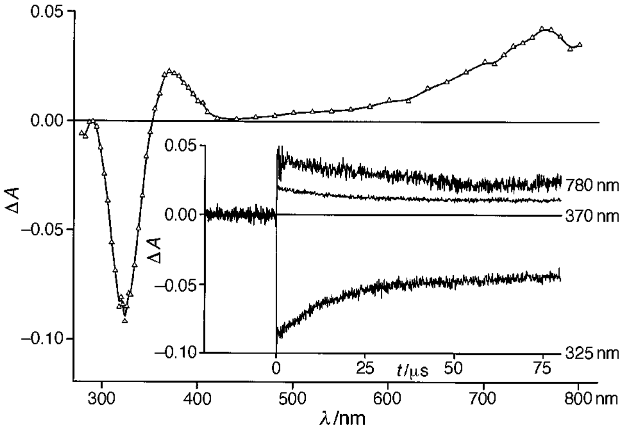

Fig. 2 Absorption difference spectrum after laser pulse photolysis of 0.1 mM $W_{10}O_{32}^{4-}$ in acetonitrile. Insert: time dependence of absorptions.

Laser flash photolysis

Fig. 2 gives an absorption difference spectrum obtained 1–5 μs after flash photolysis of $W_{10}O_{32}^{4-}$ in deaerated acetonitrile. The negative excursion for $\lambda < 355$ nm is due to the depletion of the decatungstate tetraanion. The new absorptions at higher wavelengths resemble earlier spectra obtained by Yamase and Usami[2b] at 2 ms post flash and for $590 < \lambda/\text{nm} < 900$, by Duncan *et al.*[1d] from 0.1 to 15 ns post flash and for $390 < \lambda/\text{nm} < 860$, and by Ermolenko *et al.*[3a] from 5 to 200 ns post flash and for $380 < \lambda/\text{nm} < 870$, but extend the spectral range to lower wavelengths. Results of the earlier nanosecond experiments[1d,3a] and the very small absorption around 450 nm in our spectrum show that the new absorptions are not due to the reactive excited state $W_{10}O_{32}^{4-}*$, which also has an absorption maximum at 780 nm. The insert in Fig. 2 reveals a partial recovery of $W_{10}O_{32}^{4-}$ and a simultaneous partial decay of the new absorptions at 370 and 780 nm within about 75 μs post flash. Obviously, the absorptions at 370 and 780 nm belong to one species formed in reaction (1) which we have denoted above as $H^+W_{10}O_{32}^{5-}$. Fig. 3 shows its absorption spectrum constructed from the experimental trace with the assumptions of material balance and $\varepsilon_{780} = 7000$ M^{-1} cm^{-1}. Overlaid is the absorption spectrum of

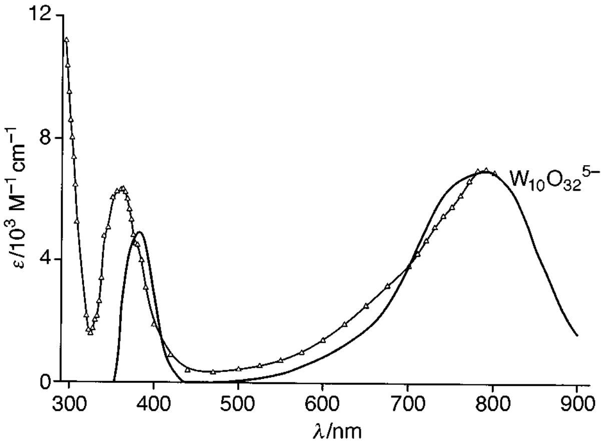

Fig. 3 Absorption spectrum of photoreduced $W_{10}O_{32}{}^{4-}$ and of electrochemically generated $W_{10}O_{32}{}^{5-}$

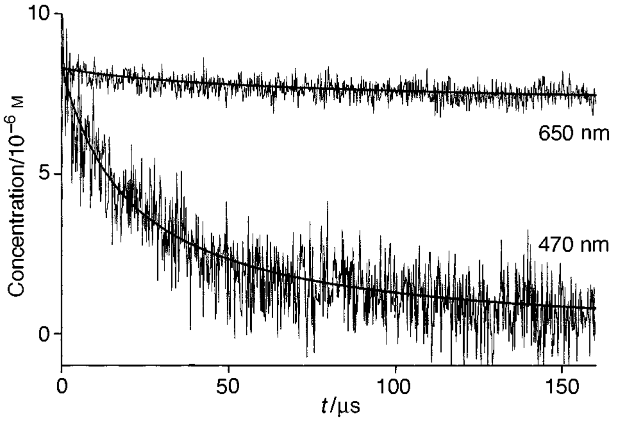

Fig. 4 Time dependence of the absorptions of $H^+W_{10}O_{32}{}^{5-}$ (650 nm) and the indenyl radical (470 nm) after laser flash photolysis of $W_{10}O_{32}{}^{4-}$ in acetonitrile containing 190 mM indene

electrochemically generated[1d] $W_{10}O_{32}{}^{5-}$. Though the spectra are similar, the differences in detail suggest that the photochemically formed species is not simply $W_{10}O_{32}{}^{5-}$.

Similar transient absorption spectra were obtained in the presence of several of the substrates of Table 1 which do not yield radicals absorbing in the 400–800 nm region. However, the absorption amplitudes, the degree of recovery of $W_{10}O_{32}{}^{4-}$ and the partial decay of $H^+W_{10}O_{32}{}^{5-}$ differed remarkably from system to system as will be outlined below. Addition of a 60-fold excess of trifluoroacetic acid to acetonitrile solutions increased the intensity of the new absorptions but did not change their spectral features. This agrees with the reported higher photoreactivity[1c] of $H^+W_{10}O_{32}{}^{4-}$.

For several substrates giving radicals with long wavelength absorptions the time dependencies of the concentrations of the transient and the persistent species could be observed simultaneously, and one example is presented here. For indene as substrate, CW-EPR experiments ensured the formation of the transient indenyl radical with usual spectral parameters[14] and of $H^+W_{10}O_{32}{}^{5-}$ by reaction (1). The concentration ratio was [Y]/[R] ≈ 700, *i.e.* similar to usual values (Table 1). The absorption of indenyl[15] was observed in the 400–480 nm region by laser flash photolysis. Fig. 4 shows two kinetic traces. The upper is due to $H^+W_{10}O_{32}{}^{5-}$ and was obtained at 650 nm, where $\varepsilon(H^+W_{10}O_{32}{}^{5-}) = 2545$ M^{-1} cm^{-1}. The lower was taken at 470 nm, corrected for the small contribution of $H^+W_{10}O_{32}{}^{5-}$ ($\varepsilon = 335$ M^{-1} cm^{-1}) and converted with ε(indenyl, 470 nm)[15] = 600 M^{-1} cm^{-1} to the indenyl radical concentration. As expected from the reaction kinetic [reactions (9) and (10)] the transient indenyl radical decays completely in the observation period while $H^+W_{10}O_{32}{}^{5-}$ decays only partially and less than in Fig. 2. From the partial decay and equation (11), the ratio of rate constants $k_x/k_{tR} = 0.055$ is estimated. The solid lines in Fig. 4 are best fits of numerical solutions of equations (9) and represent $2k_{tR} = 5.5 \times 10^9$ M^{-1} s^{-1} and $k_x = 3 \times 10^8$ M^{-1} s^{-1}. The value of $2k_{tR}$ is as expected[15] and close to the diffusion controlled limit, but the rate constant for the cross-reaction (2) is lower.

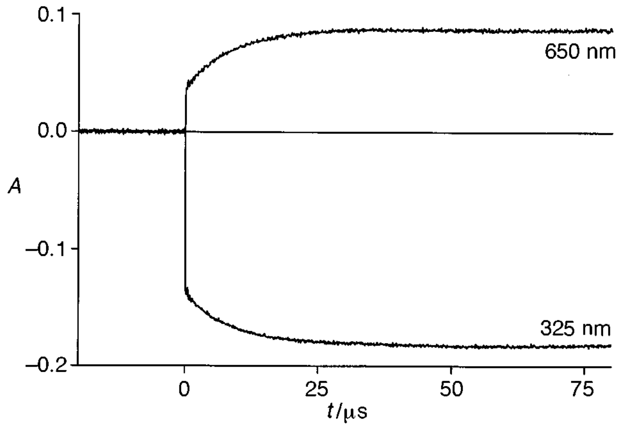

Fig. 5 Time dependence of the absorptions of $H^+W_{10}O_{32}{}^{5-}$ (650 nm) and $W_{10}O_{32}{}^{4-}$ (325 nm) after laser flash photolysis of $W_{10}O_{32}{}^{4-}$ in acetonitrile containing 4 vol% propan-2-ol

The partial decay of $H^+W_{10}O_{32}{}^{5-}$ was weaker than that in neat acetonitrile (Fig. 2) also for the substrates toluene ($k_x/2k_{tR} = 0.158$), diphenylmethane ($k_x/2k_{tR} = 0.233$), 9,10-dihydroanthracene ($k_x/2k_{tR} = 0.073$) and cyclopentane ($k_x/2k_{tR} = 0.03$). For the neat solvent, Fig. 2 shows that $k_x/2k_{tR} = 0.50$, and with *tert*-butyl alcohol as substrate, also a high $k_x/2k_{tR} = 0.30$ was obtained. Since rate constants for the self-termination of the transient radicals are not expected to differ grossly, the rate constant of the cross-reaction (2) must be strongly substrate dependent, and this may influence the efficiency of the catalytic processes.

Direct evidence for the oxidation reaction (12) of an hydroxyalkyl radical by $W_{10}O_{32}{}^{4-}$ was obtained with the substrate propan-2-ol. Fig. 5 shows the time dependencies of the absorptions of $H^+W_{10}O_{32}{}^{5-}$ and $W_{10}O_{32}{}^{4-}$ after the laser flash. Instead of a partial decay of $H^+W_{10}O_{32}{}^{5-}$ and a partial recovery of $W_{10}O_{32}{}^{4-}$, as in the Figs. 2 and 4, one notices a further increase of the former species by about a factor of two and a decrease of the latter. This indicates that reaction (12) is nearly quantitative for this case. The half-life of the process is about 10 μs of 0.1 mM $W_{10}O_{32}{}^{4-}$ and means that reaction (12) occurs at a close to diffusion controlled rate. As expected from the EPR results, for the substrate methanol no clear increase in $H^+W_{10}O_{32}{}^{5-}$ was observed.

Conclusions

We have shown that the high selectivity for product formation by radical cross-disproportionations in the photoreactions of $W_{10}O_{32}{}^{4-}$ is due to the persistency of the $H^+W_{10}O_{32}{}^{5-}$ intermediate and that the reactions follow the principles of the Persistent Radical Effect. Furthermore, an oxidation reaction of hydroxyalkyl radicals was found to be important, and several absolute and relative rate constants for the elementary reaction steps were derived. It is known that a variety of other polyoxometalates undergo very similar reactions to those described here,[2a,16] and we suggest that the Persistent Radical Effect operates there as well.

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