tamination of the sample with organic material, which resulted in the formation of a black substance with a g = 2.002. The I_2-doped samples were also prepared in this fashion.

Bromine and iodine were obtained from Baker, and both were used without further purification.

The ESR spectra were obtained on a Varian E-12 spectrometer, equipped with a dual cavity. One cavity contained a reference sample while the other, fitted with a V-4510 variable-temperature accessory, contained the sulfur sample. Temperatures were measured by placing a chromel–alumel thermocouple into the stack of the Dewar just above the active portion of the cavity and are accurate to ±0.5 °C.

During an experiment the temperature of the sample was raised to >200 °C and then lowered in increments, allowing about 15 m for equilibration before taking data at each new temperature.

The two samples used for quantitative comparisons were prepared in such a way that they occupied close to identical volumes in the cavity. The level of sulfur in the tubes was chosen such that the samples extended throughout the entire active region of the cavity and the two samples were made from the same ground and polished tube. A sample of DPPH dissolved in benzene was used as a reference to allow for correction of any change in the spectrometer's sensitivity during, or between, runs. To obtain an estimate of the signal intensity in absolute concentration units a Varian Co. 0.00033% pitch in KCl sample containing ~ 10^{13} spins per centimeter of length was placed in the sample portion of the cavity and compared to the reference signal under conditions equivalent to those used for examination of the sulfur samples.

Peak areas were obtained by numerically integrating the equation for a Lorentzian line of the measured heights and widths. Relative areas are corrected both for error in the attenuator of the spectrometer 100-kHz receiver and for Curie law variation in signal strength with temperature. Estimates of error in the relative spin concentrations vary with signal intensity from ±2% or 3% at temperatures above 200 °C to 15–20% at 160 °C. Absolute spin concentrations are believed to be within a factor of ~5 of the true value.

Conclusion

In conclusion we have observed that the presence of halogen dopants in sulfur produces a marked change in the ESR signal intensity below the polymerization transition temperature. Our measurements indicate the presence of free radical ends in doped sulfur, above and below T_p, in concentrations comparable to those above T_p in pure sulfur. We also have obtained experimental evidence for the expected sharp decrease in the concentration of free radical ends below T_p in pure sulfur. The simple equilibrium theory proposed here provides an adequate description for the observed ESR signal intensity in both pure sulfur and sulfur doped with bromine. Our original assumption that all of the bromine dissociates and bonds to sulfur appears to be justified for Br_2 concentrations of about 10^{-2} by the good agreement with the qualitative features of the data.

We have also offered, in the way of a heuristic explanation, the observation that the radical ends can be interpreted as dissociated in pure sulfur above T_p where the polymer chains are very long while the radical ends in doped sulfur are free and independent both above and below T_p.

Acknowledgment. This research was supported by NSF Grants CHE 81-19247 and CHE 78-25188. Helpful conversations with R. L. Scott are gratefully acknowledged.

Note Added in Proof. A referee has informed us that the thesis of Koningsberger[17] discusses the ESR of halogen-doped liquid sulfur. The observations are similar to those reported here. We thank Professor R. Steudel for making a copy of the thesis available.

Registry No. S, 7704-34-9; Br_2, 7726-95-6; I_2, 7553-56-2.

(17) D. C. Koningsberger, Thesis, T. H. Eindhoven, The Netherlands, 1971.

Intermediates in the Reduction of 5-Halouracils by e_{aq}^-[1]

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The radical anions of 5-bromo- and 5-iodouracil produced by the reaction of e_{aq}^- with the halouracils have been observed in nanosecond pulse radiolysis experiments by their optical absorption at 330 nm. They decay with half-periods of 7.0 ± 0.5 and 1.7 ± 0.3 ns. These short lifetimes contrast with the much longer periods observed for the electron adducts to 5-chloro- and 5-fluorouracil (4.9 and >15 μs). The uracilyl radical produced by halide elimination from the radical anions has an extinction coefficient not greater than 150 M^{-1} cm^{-1} at 330 nm and no appreciable absorption at wavelengths longer than 310 nm but reacts with 5-bromouracil to form an addition product which has a broad absorption at 365 nm. The rate constant for this latter reaction, (2.66 ± 0.09) × 10^8 M^{-1} s^{-1}, provides a reference against which to compare the rates of competing reactions. The absolute rate constant for abstraction of hydrogen from *tert*-butyl alcohol by uracilyl radical has been determined to be (2.3 ± 0.2) × 10^7 M^{-1} s^{-1}. It is clear that uracilyl radical reacts very rapidly by both addition and abstraction processes, reflecting the σ character of this radical.

The radiation chemistry of 5-bromouracil was examined by a number of investigators during the late 1960s[2] because of interest in using this moiety to localize the site of radiation damage in radiobiological studies by selective

0022-3654/83/2087-3966$01.50/0

attack of e_{aq}^- on DNA where it had replaced thymine. The principal conclusions from the various studies on the radiation chemistry of halouracils have been summarized.[3] It is known that while the anion radicals produced by reaction of e_{aq}^- with chloro- and fluorouracil in neutral aqueous solutions have lifetimes greater than microseconds that produced by reduction of bromouracil decays at much shorter times, presumably as the result of elimination of bromide ion and the concomitant formation of uracilyl radical. In the presence of a suitable hydrogen donor bromide and uracil are produced essentially quantitatively. The reaction kinetics of uracilyl radical are of particular interest since this radical's unpaired electron is expected to be localized at C_5 in a σ orbital. As a result the reactivity of this radical should be high and similar to that of phenyl radical[4] but absolute rate information is not yet available. Improvements in the time response and sensitivity of optical pulse radiolysis methods since the various earlier studies now make it possible to examine these radiolytic reduction processes in more detail. In particular, we have been able to detect the bromouracil radical anion by its absorption at 330 nm and find that it decays with a half-period of 7.0 ns, 3 orders of magnitude more rapidly than does the chlorouracil radical anion. The iodouracil radical anion is found to decay even more rapidly. The details of these investigations are reported here along with studies of the kinetics of the reactions of uracilyl radical which show that this radical is, in fact, about as reactive as phenyl radical.[4]

Experimental Section

Optical pulse radiolysis methods were largely as described in various recent publications from these laboratories[5,6] A 5-ns pulse of 8-MeV electrons from a linear accelerator was used to produce an initial concentration of $\sim 2 \times 10^{-6}$ M of the reduced species. Dosimetry was via a secondary emission monitor calibrated relative to the absorbance of $(SCN)_2^-$ at 473 nm as measured in N_2O-saturated 10 mM KSCN with the product of yield and extinction coefficient taken as 46 400 G units M^{-1} cm^{-1}.[7] Irradiations were in a 1-cm flow-through cell with a fresh solution being used for each pulse. The signals were recorded by using either a Biomation 8100 or 6500 transient recorder and processed on the Radiation Laboratory's computerized data collection system as previously described.[5,8] Because the signal-to-noise ratio available in most of these experiments was poor, extensive use was made of signal averaging. For the very fast experiments there is a significant amount of electrical noise which is synchronized with the beam and therefore contributes a background signal. It was recorded by irradiating 1 M $HClO_4$ under the conditions used in the other experiments and subtracted. This approach also effectively corrects for the Cerenkov emission which, at 330 nm, is comparable in intensity to the other signals.

Aqueous solutions were buffered at pH 7 with KH_2PO_4/K_2HPO_4 and were purged with N_2 or, where OH chemistry was to be examined, purged and saturated with N_2O. The halouracils were used as obtained (iodo- and bromouracil from Aldrich, chlorouracil from Calbiochem, fluorouracil from Sigma). *tert*-Butyl alcohol was Baker analyzed, as were H_2O_2 and the phosphate buffers.

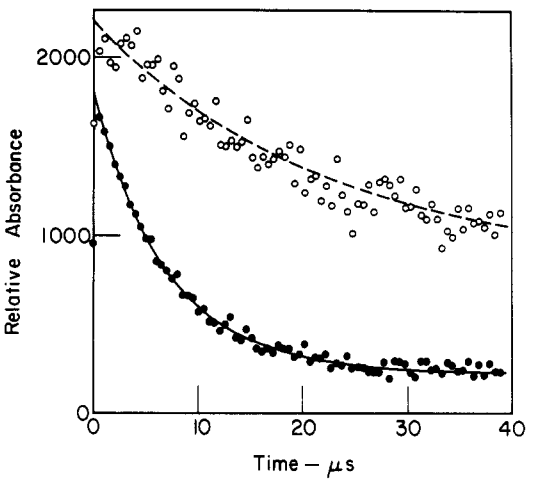

Figure 1. Decay of (O; 14 experiments) fluoro- and (●; 100 experiments) chlorouracil radical anions at pH 7 (10^{-1} M phosphate buffer) in the presence of 0.5 M *tert*-butyl alcohol (10^{-3} M halouracil, N_2 purged) as observed at 330 nm. Decay half-periods corresponding to the solid curves are 4.9 and 15.6 μs for the chlorouracil and fluorouracil radical anions but the latter is complicated by a strong residual absorption.

Results and Discussion

Preliminary experiments on halouracil solutions, where N_2O and *tert*-butyl alcohol were used to remove the radical intermediates, showed a transient signal in the region below 330 nm. This signal results from rapid deprotonation of the neutral form of the halouracil by the hydroxide produced in the radiolysis.[9] Experiments on solutions buffered with 0.1 M each of KH_2PO_4 and K_2HPO_4 (pH 6.9) showed no residual signal from this source so that most subsequent experiments were carried out at high buffer concentrations. Buffering was unimportant at wavelengths greater than 330 nm where the extinction coefficient of the basic form of the halouracils is sufficiently small (<50 M^{-1} cm^{-1}) that it cannot contribute significantly to the transient signals. Each of the halouracils was shown (at 550 nm) to react with e_{aq}^-

$$UrX + e_{aq}^- \xrightarrow{k_1} UrX^- \qquad (1)$$

with a rate constant $\sim 1.6 \times 10^{10}$ M^{-1} s^{-1}, in agreement with previously reported values.[10] In the case of bromouracil the rate of this reaction was found to be unaffected by addition of the buffer, presumably because the bromouracil at pH 7 is present predominantly in the neutral form (pK_a = 8.1).

Radiolytic reduction of fluoro- or chlorouracil in the presence of *tert*-butyl alcohol (to remove OH) produces a transient signal in the region of 330 nm which can be ascribed to the radical anion produced in reaction 1. The time dependences of these signals are illustrated in Figure 1. In the presence of 0.1 M phosphate buffer, the chlorouracil radical anion decays with a half-period of 4.9 μs, in agreement with the observations of Patterson and Bansal[10] and of Wagner and Schulte-Frohlinde.[11] This decay is largely attributable to loss of chloride from the

(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2425 from the Notre Dame Radiation Laboratory.
(2) See: Zimbrick, J. E.; Ward, J. F.; Myers, L. S. *Int. J. Radiat. Biol. Relat. Stud. Phys., Chem. Med.* **1969**, *16*, 505 for a summary of early work on this subject.
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(11) Wagner, B. O.; Schulte-Frohlinde, D. *Ber. Bunsenges. Phys.* **1975**, *79*, 589.

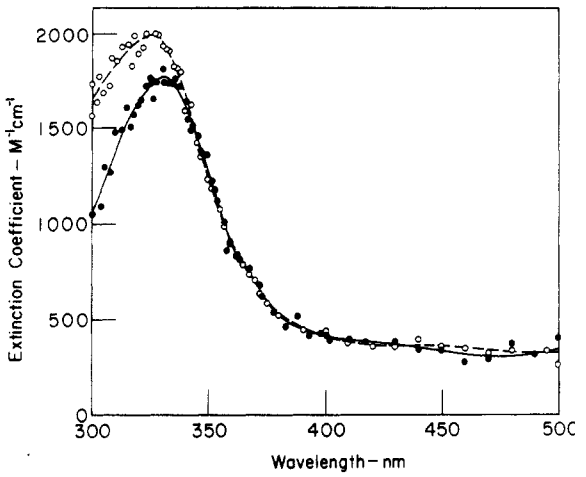

Figure 2. Absorption spectrum of (O) fluoro- and (●) chlorouracil radical anions as observed at 500 ns. Experimental conditions are as in Figure 1.

radical anion since chloride[12] and uracilyl radical[3] are produced essentially quantitatively. At a pH of 7 protonation by reaction with water or the buffer has only a minor importance. The lifetime of the fluorouracil radical anion is considerably longer (>15 μs) and appears to be controlled primarily by protonation reactions since product analysis shows that uracil is only a minor product.[3] Decay of its absorption, although faster than expected for second-order processes, leaves a residual signal indicating that the anion reacts to produce products other than fluoride and uracilyl radical. The measured decay period is, therefore, only a lower limit to the intrinsic period for fluoride elimination.

The spectra of the fluoro- and chlorouracil radical anions are given in Figure 2. Saturation of these solutions with N_2O shows that H and OH reaction products contribute to only a very minor extent. The extinction coefficients given in Figure 2 are based on a radical anion yield of 2.82 for scavenging of electrons in solutions 10^{-3} M in the halouracils.[13] These spectra are essentially as obtained by Patterson and Bansal[10] and exhibit maxima in the region of 330 nm with extinction coefficients, respectively, of 1950 and 1750 M^{-1} cm^{-1} for the fluoro and chloro derivatives. Above 340 nm the spectra are essentially identical. While loss of the halouracil contributes to the absorption difference at wavelengths below 315 nm, there will be little effect at longer wavelengths where the extinction coefficients of the halouracils at pH 7 are <100 M^{-1} cm^{-1}. Comparable experiments with 2 mM bromouracil in the presence of 0.5 M *tert*-butyl alcohol show no residual absorption (<100 M^{-1} cm^{-1}) which can be attributed to the radical anion or other reaction products at wavelengths longer than 310 nm after decay of e_{aq}^- is complete (~200 ns). If we assume that the absorption of the bromouracil radical anion is comparable to that observed for the fluoride and chloride, then it is clear that its lifetime must be less than ~25 ns. Since uracilyl radical is produced essentially quantitatively,[3] decay appears to be via very rapid bromide elimination

$$UrX^- \xrightarrow{k_2} Ur\cdot + X^- \qquad (2)$$

as has generally been assumed by most previous investigators.

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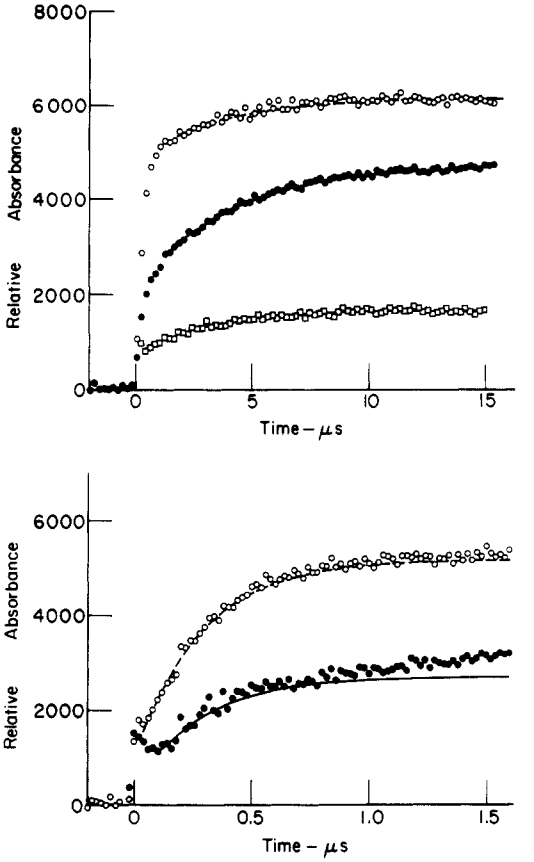

Figure 3. Time dependence of absorbance as observed at (O) 330 at (●) 365 nm for a solution 10^{-3} M in bromouracil at pH 7 (0.1 M phosphate buffer, N_2 purged) in the absence of *tert*-butyl alcohol and (□) at 365 nm in the presence of 20 mM *tert*-butyl alcohol (time scale ×2).

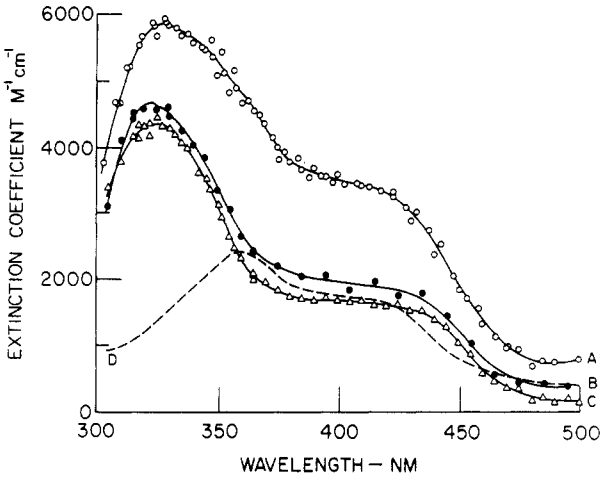

Figure 4. Absorption spectrum (A; O) as observed at ~10 μs and (B; ●) at ~0.5 μs for the experiments of Figure 3. (C, △) is the spectrum of the oxidation product as observed after saturating the solution with N_2O (scaled by 0.52). The difference between A and B (scaled by 1.17 to correct for reaction at 0.5 μs) is given by curve D and attributed to the radical adduct. Extinction coefficients are based on yields of 2.8 for the individual radicals.

Irradiation of a 1 mM bromouracil solution in the absence of an OH scavenger shows two secondary intermediates that are produced with periods of 0.2 and 3 μs, as is illustrated in Figure 3. The spectrum observed at ~0.5 μs, where reaction of e_{aq}^- and growth of the first of these secondary intermediates are essentially complete, is given by B in Figure 4. This spectrum is very similar to that observed on saturation of the solution with N_2O (C) and can be attributed to the radical produced by oxidative

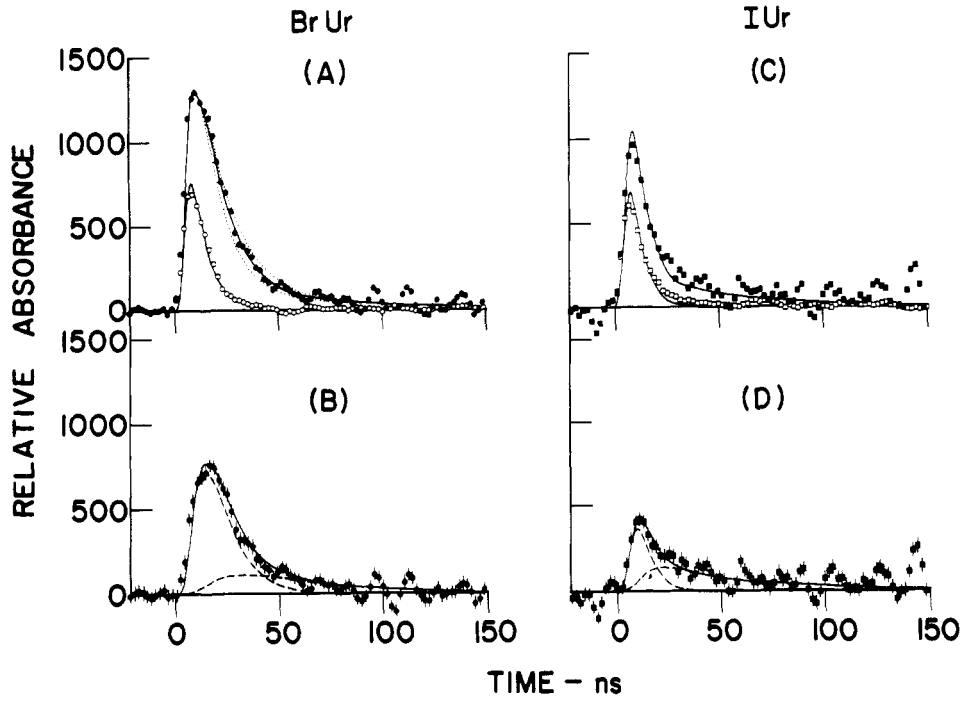

Figure 5. Time dependence of absorbance as observed at 330 nm for (●) 0.09 M bromouracil and (■) 0.10 M iodouracil at pH 7 (0.1 M phosphate buffer, N_2 purged) in the presence of 1.0 M *tert*-butyl alcohol. The contributions of e_{aq}^-, as observed at 550 nm and scaled by a factor of 0.122, are given by O and □ in A and C, and the excess signal by ◆ and ◆ in B and D. Solid curves are calculated by numerical integration methods as described in the text and are based on extinction coefficients of 1550 M^{-1} cm^{-1} and lifetimes of 6.5 and 1.7 ns, respectively, for the bromo- and iodouracil radical anions. A small contribution (E = 150 M^{-1} cm^{-1}) for the uracilyl radical ($t_{1/2}$ = 30 ns) is also included. The dotted curves in A illustrate calculations with anion lifetimes of 5 and 8 ns (see text). The dashed curves in B and D give the contributions from the anions and uracilyl radical.

dehydrohalogenation of the bromouracil, as is shown by ESR experiments,[14] along with a small contribution (~15%) from the second intermediate. In these experiments there is no evidence for any appreciable absorption attributable to the uracilyl radical. We estimate that any absorption greater than ~200 M^{-1} cm^{-1} would contribute observably to the difference between B and C. Uracilyl radical should have a spectrum red shifted from that of uracil and absorb more intensely at somewhat shorter wavelengths but this absorption apparently lies under that of the bromouracil (λ_{max} = 272 nm) which itself is somewhat red shifted from uracil (λ_{max} = 257 nm).

The spectrum observed after reactions of the initial transients are complete (at 15 μs) is given by A in Figure 4 and the difference between A and B (scaled to correct for the estimated 15% reaction at 0.5 μs) as curve D. Both of these transients virtually disappear on addition of 0.5 M *tert*-butyl alcohol, leaving only a very small residual absorbance which is mostly attributable to incomplete scavenging of the other radicals by the alcohol. It is apparent from these observations that the uracilyl radical produced in reaction 2 subsequently reacts with the substrate

$$\text{Ur}\cdot + \text{UrX} \xrightarrow{k_3} \text{adducts} \qquad (3)$$

to give what we assume is a mixture of radical adducts, represented by spectrum D in Figure 4. From observations at 365 nm it is found that the pseudo-first-order rate constant for formation of these adducts is linear in the bromouracil concentration over the concentration range of 0.5–4 mM. The observed proportionality corresponds to a second-order rate constant for reaction 3 of (2.66 ± 0.09) × 10^8 M^{-1} s^-. Attempts to selectively remove OH by using *tert*-butyl alcohol were unsuccessful because, as described below, the uracilyl radical also reacts rapidly with the alcohol, presumably by H atom abstraction.

$$\text{Ur}\cdot + \text{RH} \xrightarrow{k_4} \text{UrH} + \text{R}\cdot \qquad (4)$$

One cannot, therefore, use the usual scavenging approaches to isolate uracilyl radical to obtain its absorption spectrum.

A 0.3 mM chlorouracil solution exhibits a delayed growth in the absorption at 360 nm with a period ~12 μs. This growth appears to be a manifestation of reaction 3 with the delay (~10 μs) resulting from the time required for buildup of the uracilyl radical. From the apparent period we estimate a rate constant of 2 × 10^8 M^{-1} s^{-1} but this value will be a lower limit since kinetic analysis of the trace is complicated by the continued production of uracilyl radicals during the growth period and the decay of the product radicals observed at longer times. At higher chlorouracil concentrations the rate of the formation of the adduct is expected to be controlled largely by the rate of elimination of halide from the original radical anion.

At 1 mM bromouracil the half-period for reaction with hydrated electrons is 47 ns so that one has to use considerably higher solute concentrations in any attempt to observe shorter lived intermediates. Experiments at 4 mM with 0.5 M *tert*-butyl alcohol indicated a weak and very short-lived transient absorption at 330 nm over and above that expected from e_{aq}^-. Results obtained at an even higher concentration (0.09 mM bromouracil with 1 M *tert*-butyl alcohol; 500 experiments) are reported in Figure 5A. The very small contribution expected from oxidation by OH, as determined with 0.1 H_2O_2 added, has been subtracted. Also given in the figure is the contribution from the hydrated electron as determined on the same solution at 550 nm and scaled by a factor of 0.122 (corresponding to extinction coefficients of 1190 and 9750 M^{-1} cm^{-1} at 330 and 550 nm) to take into account the relative absorbances at the two wavelengths as determined in pure water. There is a substantial excess absorption, given in Figure 5B,

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which decays with a period ~10 ns. Since this decay is much more rapid than can be attributed to the loss of uracilyl radical by reaction with the alcohol (~30 ns at 1 M from the measurements reported below), uracilyl radical cannot be responsible and it is almost certain that this excess absorption is principally due to the bromouracil radical anion. This conclusion is confirmed by the lack of a comparable absorption in the iodouracil experiment described below. A brief scan of the spectrum indicated that 330 nm was about optimum for the kinetic measurements with the excess absorption falling off rapidly at longer wavelengths. Although one might expect some shift toward the red, the absorption spectrum of this intermediate qualitatively resembles that of the chloro- and fluorouracil radical anions in both shape and intensity. Because of the very extensive signal averaging required (at least several hundred experiments at each wavelength) we did not attempt to obtain a detailed spectrum.

Since a series of consecutive pseudo-first-order reactions are involved, the radical anion concentration in the absence of other complications is given as a function of time after production of e_{aq}^- by

$$[BrUr^-]_t = [e_{aq}^-]_0 \frac{k_1[BrUr]}{k_2 - k_1[BrUr]} (e^{-k_1[BrUr]t} - e^{k_2 t}) \quad (5)$$

where k_1 and k_2 are respectively the second-order rate constant for reaction of e_{aq}^- with the bromouracil and the first-order rate constant for decay of the radical anion. If instrumental factors were not involved, the maximum signal would be reached at $t_{max} = t_{1/2} \ln (f)/((f - 1) \ln (2))$ where $t_{1/2}$ is the half-period for reaction 1 and f is the ratio of this period to that for decay of the anion. For the 9 mM bromouracil solution, where $t_{1/2} = 4.9$ ns, the maximum of the secondary intermediate occurs ~10 ns after the maximum in the Cerenkov signal (corresponding to $f \sim 0.5$), indicating a half-life for decay of the radical anion also of the magnitude of 10 ns. More importantly, with this rapid a decay the maximum concentration of the secondary intermediate is estimated from eq 5 to be only ~45% of the total e_{aq}^- produced. Using this factor the extinction coefficient of the intermediate is estimated from the absorbance observed at 330 nm to be ~1700 M^{-1} cm^{-1} or about as observed for the fluoro- and chlorouracil anion radicals.

We have used numerical integration methods to simulate the growth and decay of the signals at the different wavelengths. All of the parameters required for calculation of the time dependence of the signal of e_{aq}^- (as observed at 550 nm) are available from external measurements.[6] Assuming that the bromouracil anion radical is the only additional contributor at 330 nm two additional parameters are required for calculation of the total signal in Figure 5A, i.e., the absorbance of this intermediate relative to that of e_{aq}^- and the period for its decay. The experiments on iodouracil described below indicate that uracilyl radical produced in reaction 2 may contribute slightly so we have included in the numerical model a term to take this into account assuming an extinction coefficient of 150 M^{-1} cm^{-1} and a reaction period of 30 ns. Simulations based on such a model show that, where the periods for the growth and decay of the radical anion are comparable, the signal at the maximum is predominantly due to the initial intermediate and rather insensitive to the decay period for reaction 2. With the latter in the region of 8–10 ns the maximum can be fitted quite well if we take the extinction coefficient of the radical anion as 1.30 times that of e_{aq}^- (corresponding to 1550 M^{-1} cm^{-1}, i.e., comparable to but slightly smaller than that observed for the fluoro and chloro analogues). With this parameter fixed the data in the region of 30 ns (i.e., at 50% of the maximum) are fitted very well with the half-period for decay of the anion taken as 6.5 ns (upper solid curve in Figure 5A). The dotted curves illustrate results calculated for periods of 5 and 8 ns with the extinction coefficients of the radical anions adjusted (1675 and 1450 M^{-1} cm^{-1}, respectively) to give a maximum in the net signal as indicated in Figure 5B. It is seen that interpretation of the data depends much more crucially on the timing of the decay than on the shape of the curve. The differences between the signal observed at 330 nm and the contribution ascribable to e_{aq}^- is given in Figure 5B along with the corresponding simulation. The latter includes components for both the radical anion and the uracilyl radical as indicated by the dashed curves. If the latter is deleted from the simulations, then one must increase the anion lifetime to ~7.5 ns to fit the data in the decay region. We conclude that the decay period for the bromouracil radical anion is 7.0 ± 0.5 ns.

Data from similar experiments on a 10 mM iodouracil solution containing 1 M *tert*-butyl alcohol are also reported in C and D of Figure 5. The excess absorption over that ascribable to the hydrated electron is considerably less than for the bromouracil, as would be expected since the iodouracil radical anion can be presumed to have an even shorter lifetime than the bromide. Experiments on iodouracil solutions containing *tert*-butyl alcohol as a proton donor show that the yield of uracil measured by liquid chromatographic methods is comparable to that observed from the bromide (~2.8)[3] so that there is little question but that uracilyl radical is produced essentially quantitatively. The excess absorption observed in Figure 5D gives an upper limit to the possible contribution from uracilyl radical in the bromouracil experiment. However, it is more likely attributable to iodouracil radical anion, since the lifetime is shorter than expected for uracilyl radical. The area under curve D is 20–30% of the area under curve B, indicating a lifetime between 1.4 and 2.0 ns if the extinction coefficient is similar to that of the bromouracil radical anion. If we assume an extinction coefficient of 1550 M^{-1} cm^{-1} and a lifetime of 2 ns, numerical integrations similar to those used in the case of bromouracil give a maximum level about as observed. Somewhat of a tail on the absorption is, however, noticeable in the region of 20–50 ns which is not reproduced in these simulations. While this tail is barely above the noise level, it appears in the individual recordings and does indicate that uracilyl may be contributing to a very small extent. Taking the lifetime of uracilyl radical in the presence of 1 M *tert*-butyl alcohol as 30 ns, as given by the rate constant of 2.3×10^7 M^{-1} s^{-1} determined below, its extinction coefficient cannot significantly exceed 150 M^{-1} cm^{-1} at 330 nm and it cannot contribute more than ~20% to the net absorption observed at 10 ns. A simulation based on a radical anion lifetime of 1.7 ns and extinction coefficient of 1550 M^{-1} cm^{-1} and uracilyl radical lifetime of 30 ns and extinction coefficient of 150 M^{-1} cm^{-1} is given by the solid curve in Figure 5D, with the individual components indicated by the dashed curves. A contribution of the magnitude of the uracilyl radical absorption included in the present calculations would be completely masked in the various other experiments that we have carried out and it is clear that, unless a source of uracilyl which does not absorb in the region of 270–300 nm is found, direct studies of its reaction kinetics will be virtually impossible.

In view of the 3 orders of magnitude difference between the lifetimes of the chloro- and bromouracil radical anions one would expect a larger difference between the bromide

Figure 6. Dependence on the pseudo-first-order rate constant for the growth of the adduct on *tert*-butyl alcohol concentration. The linear increase indicated corresponds to a rate constant of 2.3×10^7 M^{-1} s^{-1} for reaction of uracilyl radical with the alcohol.

and iodide than is noted here. However, if the lifetime in the case of iodouracil is appreciably shorter than 1 ns, there would not be any observable contribution to the trace. Upon addition of 0.1 M H_2O_2 to remove e_{aq}^- only a very small signal, which does not decay, is observed and this can be attributed to oxidation of the iodouracil by ~5% of the OH radicals not scavenged by the *tert*-butyl alcohol. The additional absorption must, therefore, represent a reduction product which is almost certainly the iodouracil radical anion. Apparently its lifetime is approaching some sort of a lower limit representing the possible frequency for dissociation of the $C-I^-$ bond in solution even though the indicated frequency, $\sim 10^9$ s^{-1} is still considerably lower than the preexponential factors usually given for first-order processes.

From measurements of the dependence of uracil production on the relative concentrations of *tert*-butyl alcohol and bromouracil, Bhatia and Schuler[3] concluded that the ratio of the rate constants for reaction 3 and 4 was 1.3. The present more direct experiments show that the ratio must be somewhat smaller. For example, addition of 1 mM *tert*-butyl alcohol to 1 mM bromouracil has very little effect on the period for reaction 3 (a decrease from 2.66 to 2.38 μs was noted) or on the magnitude of the signal. In the present study we have used reaction 3 to monitor the rate for abstraction of hydrogen from *tert*-butyl alcohol and conclude that the rate constant ratio k_4/k_3 is ~0.1. Since this ratio is almost identical with the ratio of the rate constants for reaction of OH with *tert*-butyl alcohol and bromouracil, one cannot use *tert*-butyl alcohol to selectively remove either of these intermediates.

The time dependence of the signal observed at 365 nm for a 1 mM solution containing 20 mM *tert*-butyl alcohol is given in Figure 3. The half-period of the component corresponding to reaction 3 is 0.95 μs as compared with 2.66 μs in the absence of *tert*-butyl alcohol. The contribution of reaction 4 to the observed pseudo-first-order rate constant is, therefore, 4.7×10^5 s^{-1}, which corresponds to a second-order rate constant of 2.3×10^7 M^{-1} s^{-1}. In Figure 6 we illustrate that the contribution to the pseudo-first-order rate constant is, within experimental error, proportionate to the alcohol concentration with a slope corresponding to $k_4 = 2.3 \times 10^7$ M^{-1} s^{-1}. The competitive effect of *tert*-butyl alcohol on the limiting signal is very sensitive to corrections for the absorbance of the products resulting from oxidation by OH, which at 365 nm contributes ~50% of the signal, and for other background signals. For the solution 20 mM in *tert*-butyl alcohol the former correction was estimated by saturating the solution with N_2O and the latter was shown to be small by increasing the alcohol concentration to 0.2 M. The 20 mM *tert*-butyl alcohol reduces the signal of the uracilyl adduct by a factor of 0.38, which is, however, estimated to be accurate to only ±0.04 because of the corrections involved. This value corresponds to a ratio of rate constants of 0.08 ± 0.01. The various measurements on the rate constant for H abstraction from *tert*-butyl alcohol by uracilyl radical are summarized by a value of $(2.3 \pm 0.2) \times 10^7$ M^{-1} s^{-1} at 23 °C.

The rate constants for both addition and abstraction reactions of uracilyl radical are very high, comparable, for example, to those for reactions of H atoms and phenyl radicals and much higher than those for typical π radicals. These high rate constants are a manifestation of localization of the unpaired electron at the 5-position of the radical in an orbital having predominantly s character.

Acknowledgment. We thank Dr. L. K. Patterson for discussions on details of this research.

Registry No. 5-Bromouracil radical anion, 36684-91-0; 5-iodouracil radical anion, 36684-92-1; 5-chlorouracil radical anion, 36684-90-9; 5-fluorouracil radical anion, 36684-89-6; uracilyl radical, 15279-39-7; *tert*-butyl alcohol, 75-65-0; 5-bromouracil, 51-20-7.