

Photoreduction of 9,10-Phenanthrenequinone¹

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Abstract: The photolysis of phenanthrenequinone in 2-propanol gives rise to 9,10-phenanthrenediol and acetone. This reaction has been studied in detail using continuous and flash irradiation techniques. The quantum yield of the disappearance of phenanthrenequinone in 2-propanol-benzene mixtures is independent of the incident light intensity (435 nm) and increases with the alcohol concentration to reach a maximum value of 1.6 in pure 2-propanol. Flash photolysis revealed two transients: one, which absorbs in the 340–500-nm region, decays with second-order kinetics ($k = 8.1 \times 10^8 \text{ l. mole}^{-1} \text{ sec}^{-1}$ in benzene), and appears in all the solvents examined, is assigned as the 10-hydroxyl-9-phenanthryloxy radical; the other, which absorbs in the 500–760-nm region, decays with first-order kinetics ($k = 1 \times 10^5 \text{ sec}^{-1}$ in benzene), and appears only in benzene and glacial acetic acid, is tentatively identified as the first triplet state of phenanthrenequinone. The quantitative results are interpreted in terms of the initial formation of internally excited semiquinone radicals by hydrogen abstraction from the solvent.

A number of studies have recently been reported concerning the photochemistry of 9,10-phenanthrenequinone (PAQ).^{3–7} It was found that, with several substrates, radicals are generated which yield both 1,4-addition and 1,2-addition products. The photochemical reduction of PAQ by ethanol furnishes 9,10-phenanthrenediol and acetaldehyde in a 1:1 ratio, and the quantum yield for the disappearance of PAQ has been reported to be greater than unity.⁷ The photochemical behavior of PAQ can be expected to bear resemblance to that of the *p*-quinones, which have been extensively investigated by continuous irradiation^{7–13} and flash techniques.^{13,14} Several reports indicate that the photoreactions of *p*-quinones generally proceed *via* their triplet states,^{10–14} although in the case of duroquinone the singlet excited state is proposed to be the reactive species.¹⁴ Indeed, several of the photochemical reactions of PAQ have been interpreted in terms of the efficient population of its first triplet level.^{5,6}

The present study was undertaken with the aim of elucidating the mechanism of the photoreduction of PAQ. We have found that the irradiation of PAQ in 2-propanol leads cleanly to 9,10-phenanthrenediol and acetone and, consequently, have chosen this reaction for detailed investigation.

Experimental Section

Materials. Phenanthrenequinone (Fisher, highest purity) was purified by column chromatography and crystallized from benzene

(mp 208–209°). Anthracene (Eastman X-480) was used without further purification. The benzene (Fisher B245) used for quantum yield measurements was purified by fractional distillation with a spinning-band column. For the flash photolysis experiments, the solvent was slowly distilled from phosphorus pentoxide through a 4-ft glass-bead-packed column. The fraction of distillate used in the photochemical experiments was shown to be free of the initial impurities by glpc (Triton X-305 on Chromosorb P). It was established that 2-propanol (glass distilled, Burdick and Jackson Laboratories, Inc.), and glacial acetic acid (Fisher Reagent) could be used without further purification.

Photoreduction Products. Shaking a colorless, completely photolyzed solution of PAQ in 2-propanol in air caused the slow regeneration of the characteristic yellow color of the quinone. When a single microcrystal of potassium permanganate was added to this solution, 92% of the PAQ was rapidly regenerated. Acetone in an amount approximately equal to the amount of PAQ which had reacted was detected in the photolyzed solution by means of glpc (Triton X-305 on Chromosorb P).

Quantum Yield Measurements. These were performed with previously described apparatus.¹⁵ The solutions of PAQ ($4.8 \times 10^{-4} \text{ M}$) in various 2-propanol-benzene mixtures were degassed by the freeze-pump-thaw method in a side arm attached to the rectangular 1-cm path length Pyrex photolysis cells. The exciting wavelength was, in all cases, 435 nm; products due to the photolysis of PAQ do not absorb in this region.

Flash Experiments. The flash apparatus is described elsewhere.¹⁶ Solutions of PAQ ($1.4 \times 10^{-4} \text{ M}$) were degassed in the usual manner in a vessel designed for multiple fillings¹⁷ and then sealed. The 6-cm optical path length Pyrex cells were wrapped with Roscolene Filter No. 963,¹⁸ which transmits from 350 to 530 nm and thus confines irradiation to the long-wavelength PAQ band. The battery-stabilized Osram 450-W xenon arc analyzing beam was filtered through 1 cm of distilled water. Care was taken to flash each cell with the same energy (900 J) and to minimize accidental photoreaction initiated by the analyzing beam by opening the protective shutter and triggering the flash simultaneously. Only the data obtained from the first flash of each solution sample were used in the calculations. All experiments were performed at room temperature ($25 \pm 3^\circ$).

Results

Quantum Yields. The quantum yields for the reduction of PAQ in 2-propanol-benzene mixtures as a function of the solvent composition are listed in Table I.

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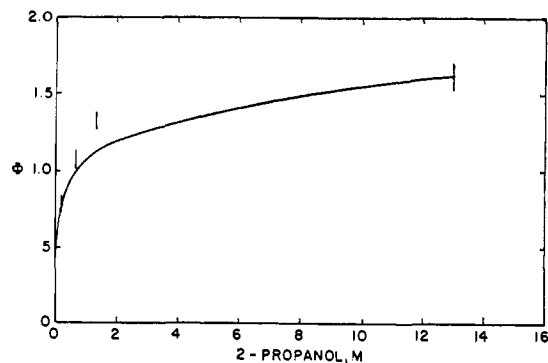


Figure 1. The quantum yield of the disappearance of PAQ (Φ) as a function of the 2-propanol concentration. The solid line is calculated with eq 10 and the points are experimental.

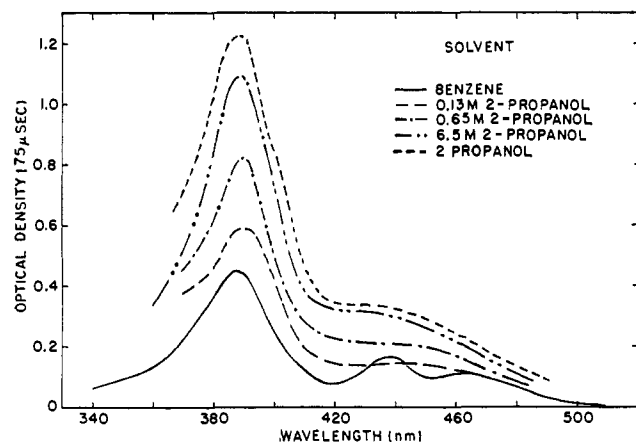


Figure 2. Transient absorption in the 340–500-nm region in 2-propanol–benzene mixtures 75 μ sec after flash irradiation.

The dependence of the quantum yield on the alcohol concentration is complex (Figure 1) and the conventional plot of the reciprocal of these quantities is not linear. Within the limits of experimental scatter, the quantum yield was found to be independent of the light intensity ($3\text{--}18 \times 10^{-7}$ einstein min^{-1}). The rate of

Table I. Quantum Yield of the Disappearance of PAQ as a Function of 2-Propanol Concentration^a

2-Propanol, <i>M</i>	Quantum yield ^b
13.07 ^c	1.62 \pm 0.07 (2)
6.54	1.35 (1)
1.31	1.33 \pm 0.05 (6)
0.65	1.07 \pm 0.03 (3)
0.13	0.79 \pm 0.05 (2)

^a 4.83×10^{-4} *M* phenanthrenequinone unless otherwise indicated. ^b Average value for the number of runs quoted in parentheses. ^c 7.63×10^{-4} *M* phenanthrenequinone.

disappearance of PAQ is directly proportional to the intensity of the light absorption, and plots of $\log(T_S^{-1} - 1) + a \log(T_S^{-1} + a)$ against time (T_S is the transmittance and a a correction factor for reflection in the apparatus)¹⁵ are linear. The quantum yields listed in Table I were obtained from the slopes of these plots.

Since PAQ is considered to react *via* its triplet state (intersystem crossing efficiency approximately unity⁶), the quenching of its reduction with anthracene was ex-

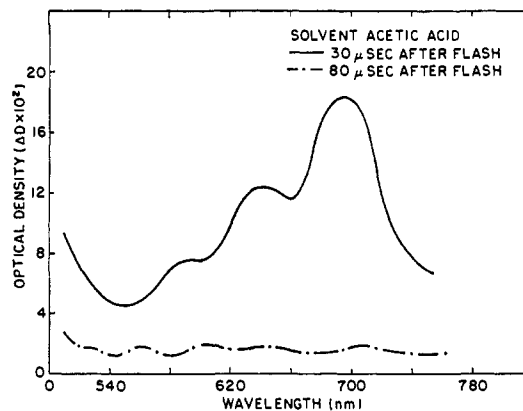


Figure 3. Transient absorption in the 500–760-nm region in glacial acetic acid.

amined. The triplet energies of anthracene and PAQ are 42.2¹⁹ and 48.8 kcal/mol,⁶ respectively. The quantum yield of PAQ reduction (6.8×10^{-4} *M*, 2-propanol) was found to be lowered by *ca.* 25% in the presence of 1.2×10^{-3} *M* anthracene. By contrast, naphthalene (triplet energy 60.8 kcal/mole²⁰) at a concentration of 9.4×10^{-3} *M* is without effect.

Transient Spectra. The flash excitation of PAQ gives rise to a transient absorption in the 340–500-nm region with all the solvents examined. There is a well-defined maximum at 390 nm and, generally, a shoulder at *ca.* 430 nm. In pure benzene, however, the absorption between 420 and 500 nm is resolved into two peaks with λ_{max} 435 and 460 nm, respectively (Figure 2). Only in acetic acid and benzene was a very short lived transient absorption with λ_{max} 700 nm observed (Figure 3). All of the 340–500-nm absorption appears to be due to the same transient species since the ratio of changes in the optical density at 390 and 430 nm ($\Delta D_{390}/\Delta D_{430}$) is invariant with the solvent and with the time after the flash excitation. The amount of this transient species increases with the 2-propanol concentration in benzene as the dilutant (Figure 2).

In an attempt to identify the reactive state of PAQ from which the transients arise, energy-transfer experiments were performed. A degassed 1.4×10^{-4} *M* solution of PAQ in benzene containing 2.8×10^{-4} *M* anthracene showed no transients due to PAQ excitation, but, instead, the 425-nm triplet–triplet absorption²¹ of anthracene was observed. A blank experiment with anthracene in the absence of PAQ produced no transient absorption whatever. This demonstration of triplet energy transfer from PAQ to anthracene indicates that both the 340–500-nm and 700-nm transients are derived from the PAQ triplet state. Similar experiments in 2-propanol showed only a slight decrease in the 390-nm absorption band and a slight enhancement at 425 nm compared to solutions without anthracene. These results are in agreement with the corresponding quantum yield measurements.

Flash excitation of aerated solutions of PAQ in benzene produced no transient absorption. On the other

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hand, solutions of PAQ in 2-propanol showed only a slight decrease in the amount of transient absorption relative to degassed samples.

Transient Kinetics. The 700-nm transient decay in glacial acetic acid and in benzene is first order for over three half-lives with rate constants of $5.4 \times 10^4 \text{ sec}^{-1}$ and $1 \times 10^5 \text{ sec}^{-1}$, respectively. Kinetic data for the 340–500-nm transient were obtained at 480 nm in order to minimize the interference from the permanent disappearance of PAQ. This transient shows second-order decay, and plots of $1/\Delta D_{480}$ against time are linear for at least 85% of the decay in every case. Values of $k_{\text{exptl}}/\epsilon_{480}$ for benzene–2-propanol mixtures are listed in Table II. An estimate of the extinction coefficient ϵ_{480}

Table II. Decay Data for the 340–500-nm Transient in Benzene–2-Propanol Mixtures

2-Propanol, <i>M</i>	$k_{\text{exptl}}^a/\epsilon_{480}$, $\text{cm sec}^{-1} \times 10^{-5}$	k_{exptl}^b l. mole ⁻¹ $\text{sec}^{-1} \times 10^{-8}$
0	4.5	8.1
0.13	7.1	12.8
0.65	5.3	9.5
6.5	4.3	7.7
13.1	2.0	3.6

^a ϵ_{480} is the molar extinction coefficient of the transient at 480 nm.

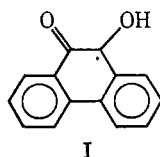
^b Lower limit based on $\epsilon_{480} \geq 1.8 \times 10^3 \text{ l. mole}^{-1} \text{ cm}^{-1}$.

was obtained by assuming at this point that this transient incorporates one molecule of PAQ and that, in pure 2-propanol, two molecules of the transient give rise to one molecule of the product, 9,10-phenanthrene-diol. This affords the lower limit of $\epsilon_{480} \geq 1.8 \times 10^3 \text{ l. mole}^{-1} \text{ cm}^{-1}$.²²

Discussion

Perhaps the most salient features of the results are that the rate of PAQ disappearance is linearly dependent on the absorbed light intensity and that the quantum yields at high 2-propanol concentrations substantially exceed unity. The first of these observations severely limits the mechanisms which may be seriously considered, for those involving bimolecular radical recombinations as the only steps yielding product lead to intensity-dependent expressions for the quantum yield.

The ease with which triplet states of ketones abstract hydrogen from appropriate reactants is well documented,²³ as is the second-order recombination of the resulting semiquinone radicals.⁵ The behavior of the 340–500-nm transient is consistent with that expected for the 10-hydroxyl-9-phenanthryloxy radical (I), and



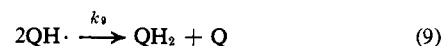
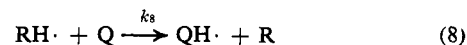
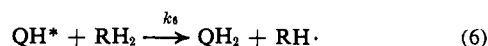
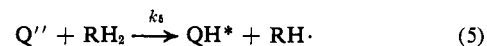
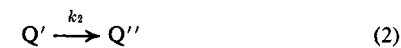
(22) The lower limit arises because this procedure overestimates the transient concentration if, as is proposed in the Discussion, part of the 9,10-phenanthrenediol arises from a reaction not involving this transient. To partially compensate for this discrepancy, the quantum yield of PAQ disappearance was taken into consideration by assuming that the maximum transient concentration = 2 (concentration of PAQ reacted)/ Φ .

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this absorption is therefore assigned to this species. It appears in all the solvents used. The second-order rate constant for the decay in benzene is $8.1 \times 10^8 \text{ l. mole}^{-1} \text{ sec}^{-1}$, whereas the diffusion-controlled rate constant at 25°, based on the Debye equation, is $1.08 \times 10^{10} \text{ l. mole}^{-1} \text{ sec}^{-1}$. Nonetheless, the variation of the rate with the solvent composition (Table II) qualitatively follows the prediction based on viscosity data²⁴ for these mixtures and the Debye equation. By way of comparison, the rate constant of $9 \times 10^8 \text{ l. mole}^{-1} \text{ sec}^{-1}$ reported by Bell and Linschitz for the recombination of the semiquinone radical derived from benzophenone in benzene may be quoted.²⁵ A similar discrepancy between experimental and calculated diffusion-controlled rate constants was reported by Burkhart for the recombination of both pentyl and benzyl radicals in fluid solution.²⁶

The short-lived transient absorption in the 700-nm region, which decays by a first-order process, is only observed in those solvents which are relatively poor hydrogen atom donors. We tentatively assign this absorption to the first triplet state of PAQ. There was no evidence that this state absorbs appreciably between 340 and 500 nm although, because of overlapping with the ground-state absorption of PAQ in this region, this possibility cannot be eliminated. It should be noted that hydrogen abstraction from benzene by photoexcited ketones may be possible.^{25, 27} Consequently, the rate constant in the 700-nm region reflects the reaction of triplet PAQ with benzene as well as its deactivation. The pseudo-first-order rate constant $\sim 10^8 \text{ sec}^{-1}$ corresponds to a lifetime of 10 μsec for the PAQ triplet and, if the reaction with benzene is presumed to predominate, a rate constant of $9 \times 10^8 \text{ l. mole}^{-1} \text{ sec}^{-1}$ for this reaction is obtained. This value is about the same as that reported for the reaction of the benzophenone triplet with benzene.²⁵

The results of the quantum yield and flash experiments lead us to propose the following simplified mechanism for the reduction of PAQ in which the formation of a vibrationally excited semiquinone radical plays a key role.



Here Q, Q', and Q'' represent the ground, first excited singlet, and first triplet states of PAQ, respectively.

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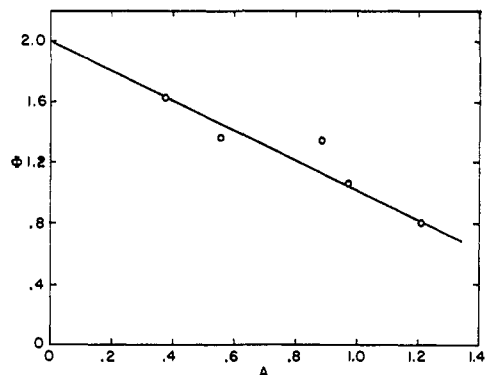


Figure 4. Plot of the quantum yield of the disappearance of PAQ (Φ) against $A = \{2k''[k' + (\text{RH}_2)] + k'(\text{RH}_2)\} / \{[k' + (\text{RH}_2)][k'' + (\text{RH}_2)]\}$.

The 2-hydroxyl-2-propyl radical is represented by $\text{RH}\cdot$, and acetone by R . In the development which follows, it is assumed that the triplet state is populated with an intersystem crossing efficiency of unity,⁶ that $k_1 = 1$ mole/einstein, and that the natural decay of the triplet state (step 3) is independent of solvent composition. Step 5, in which the vibrationally excited radical ($\text{QH}\cdot^*$) is generated, accounts for the independence of quantum yield of the light intensity. All other plausible mechanisms investigated which lead to a limiting quantum yield greater than unity, including that which considers the reaction of $\text{QH}\cdot$ with 2-propanol,⁷ yield expressions dependent upon light intensity. There is evidence that vibrationally excited species can participate in solution photochemistry.²⁸ Intermolecular hydrogen bonding between ketones and alcohols has been demonstrated²⁹ and is likely to be important for PAQ with its relatively large dipole moment (5.60 D).^{30,31} PAQ may, in its ground state, be hydrogen-bonded to two or more 2-propanol molecules and in a more detailed formulation of steps 5 to 7 the species represented by $\text{QH}\cdot^*$ could perhaps be viewed as an energetic union of a semiquinone radical and one or more 2-propanol molecules. This species would either react with the hydrogen-bonded alcohol to produce 9,10-phenanthrene-1,2-diol (QH_2 , step 6) or deactivate to $\text{QH}\cdot$ (step 7). It is central to this mechanism that the deactivated semiquinone radical $\text{QH}\cdot$ does not react further with 2-propanol, but disappears by bimolecular combination (step 9). Quantum yields greater than unity can be understood in terms of the reaction of the $\text{QH}\cdot^*$ species with 2-propanol, and of the radical $\text{RH}\cdot$ with Q (step 8). It has been noted in previous work with PAQ that there is a slow photochemical reaction even in pure benzene.^{6,27} This is almost entirely suppressed in the presence of olefins, and, because of the rapidity of the photochemical reaction of PAQ with 2-propanol, we assume this side reaction to be unimportant at alcohol concentrations $>0.1 M$ as well. We may infer that the reaction of the PAQ triplet state with the alcohol is rapid compared to deactivation (step 3), since neither

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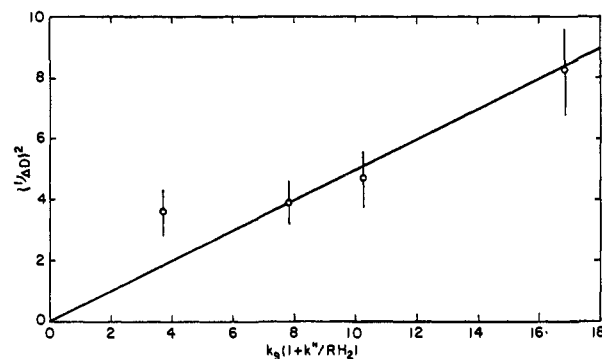


Figure 5. Plot of $(\Delta D_{\text{QH}\cdot})_{\text{max}}^{-2}$ against $k_9\{1 + [k''/(\text{RH}_2)]\}$ for data at 440 nm.

anthracene nor oxygen greatly suppresses radical formation in solutions of high 2-propanol content. In benzene, however, these reagents effectively eliminate radical formation. Since some phenanthrene-1,2-diol is formed in pure benzene as well,^{6,27} we infer that hydrogen abstraction occurs and leads to $\text{QH}\cdot$ and $\text{C}_6\text{H}_5\cdot$ radicals which react further to yield QH_2 and other products.

Application of the steady-state approximation to the various excited states and intermediates gives the quantum yield for the disappearance of PAQ (Φ) as

$$\Phi = \frac{(\text{RH}_2)[k' + 2(\text{RH}_2)]}{[k' + (\text{RH}_2)][k'' + (\text{RH}_2)]} \quad (10)$$

where $k'' = k_3/k_5$ and $k' = k_7/k_6$. The quantum yield data provide $k'' \approx 0.04$ mole/l. and $k' \approx 7.8$ mole/l., and the solid line in Figure 1 was calculated from eq 10 using these values. The fit of the mechanism is perhaps best seen if eq 10 is rewritten in the form $\Phi = 2 - A$, only where

$$A = \{2k''[k' + (\text{RH}_2)] + k'(\text{RH}_2)\} / \{[k' + (\text{RH}_2)][k'' + (\text{RH}_2)]\}$$

The plot of Φ against A shown in Figure 4 has the required intercept/slope value of -2 .

The mechanism provides the following expression for the maximum radical concentration, which is considered to be reached when the change in optical density due to the radical, $\Delta D_{\text{QH}\cdot}$, is a maximum.

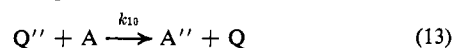
$$(\text{QH}\cdot)^2 = \frac{k_1 k_2 I_{\text{abs}} k_5 (\text{RH}_2)}{k_9 (k_2 + k_4) [k_3 + k_5 (\text{RH}_2)]} \quad (11)$$

With $k_1 = 1 \approx k_2/(k_2 + k_4)$ as before, $k_3 = k''k_5$, and with $\Delta D_{\text{QH}\cdot} \approx \epsilon_{\text{QH}\cdot}(\text{QH}\cdot)l$ applicable at wavelengths for which the extinction coefficient $\epsilon_{\text{QH}\cdot}$ of the radical is substantially greater than that of PAQ, eq 11 becomes

$$\frac{1}{(\Delta D_{\text{QH}\cdot})_{\text{max}}^2} = \frac{1}{I_{\text{abs}} \epsilon_{\text{QH}\cdot}^2 l^2} \left[k_9 + \frac{k_9 k''}{(\text{RH}_2)} \right] \quad (12)$$

where l is the pathlength of the cell. The rate constant k_9 is identified with the second-order rate constants k_{exptl} listed in Table II. A plot of the bracketed term in eq 12 against $(\Delta D_{\text{QH}\cdot})_{\text{max}}^{-2}$ is shown in Figure 5. The point corresponding to the highest 2-propanol concentration is seen to deviate substantially from the expected linear relationship. In this solution, however, the permanent bleaching of PAQ is most extensive, and consequently the simple, approximate relationship between $\Delta D_{\text{QH}\cdot}$ and the radical concentration may not be valid.

The transfer of triplet energy may be formulated as



where A and A'' are the ground and triplet states, respectively, of anthracene. With this step, the mechanism furnishes the expression

$$\frac{\Phi}{\Phi_A} = \frac{(\text{QH}\cdot)^2}{(\text{QH}\cdot)_A^2} = 1 + \frac{k_{10}(A)}{k_5[k'' + (\text{RH}_2)]} \quad (14)$$

in which Φ_A and $(\text{QH}\cdot)_A$ represent the quantum yield and radical concentration, respectively, in the presence of anthracene in pure 2-propanol. With an anthracene concentration of $1.2 \times 10^{-3} M$ the experimental values of $\Phi/\Phi_A = 1.4$ and $(\text{QH}\cdot)^2/(\text{QH}\cdot)_A^2 = 1.5$ are in satisfactory agreement. Using the value $k_{10} = 3.2 \times 10^9 \text{ l. mole}^{-1} \text{ sec}^{-1}$ at 25° , which was obtained from the Debye

equation with the assumption that the energy transfer proceeds at the diffusion-controlled rate, eq 14 affords the value $7.3 \times 10^5 \text{ l. mole}^{-1} \text{ sec}^{-1}$ for k_5 , the rate constant for the abstraction of hydrogen from 2-propanol by triplet PAQ. The effective lifetime of the triplet state in 2-propanol is therefore $1.0 \times 10^{-7} \text{ sec}$, which may be compared with the value of $1.3 \times 10^{-7} \text{ sec}$ reported by Wilkinson for the rate of hydrogen abstraction from 2-propanol by the triplet state of α -anthraquinone in a 4:1 mixture of benzene-2-propanol.¹¹

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Chemistry of Iodine-128 and Iodine-130 Recoils in Neutron-Irradiated Crystalline Potassium Iodate and Potassium Periodate¹

G. E. Boyd and Q. V. Larson

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Abstract: Radioactive iodine-128 and iodine-130 recoils formed by neutron capture in crystalline KIO_3 and KIO_4 appeared as iodide, iodate, and periodate ions on analysis of alkaline aqueous solutions of the irradiated solids. With KIO_3 more than two-thirds of the radioiodine was retained as radioiodate, and small amounts of radio-periodate were found. With KIO_4 nearly 90% of the recoils appeared as radioiodate, while the periodate retention was slightly less than 10%. The relative concentrations of the radioiodine oxidation states varied with the time and temperature of the neutron bombardment. Radioiodide was readily converted to iodate and periodate on heating or on exposing the neutron-irradiated solids to ^{60}Co γ rays. Iodine-131 added in tracer concentrations to crystalline KIO_3 or KIO_4 as iodide ion was rapidly oxidized to iodate and to periodate on heating the solids above room temperature. There was only a small isotopic effect in the yields of the iodine valence states in which ^{128}I and ^{130}I were combined.

This reinvestigation of the chemistry of radioiodine recoils formed in crystalline alkali metal iodate and periodate by thermal neutron capture was inspired by the possibility that careful measurements of the yields of the various iodine valence states might be employed in a test of the "ligand loss" hypothesis.^{2a} This hypothesis states that the chemical nature of the fragments created from a molecule-ion by a nuclear transformation is governed by the distribution of bonding electrons in the species prior to the disruptive event. Recent determinations^{2b} of the relative concentrations of the radiochlorine valence states produced by thermal neutron capture in KClO_2 , KClO_3 , and KClO_4 gave a qualitative agreement with the hypothesis. Quantitative information on the distribution of electrons in solid KIO_3 and KIO_4 has become available from Mössbauer effect studies³ and from chemical shift deter-

minations in high-resolution measurements on the energies of photoelectrons produced by X-rays in these compounds.⁴ The positive charge on the iodine atoms in KIO_3 and KIO_4 appears to be significantly larger than that on the chlorine atoms in KClO_3 and KClO_4 , respectively. According to the "ligand loss" hypothesis, the yields of radioiodine recoil valence states should differ from those for the corresponding states of recoil radiochlorine.

A second development further stimulated this research. Neutron irradiation of the very long lived ^{129}I had been known to produce a 12.5-hr iodine activity presumably directly by an (n,γ) reaction. However, recently it has been found⁵ that between one-half and two-thirds of the 12.5-hr ^{130}I was formed *via* the decay of a highly internally converted 9.2-min iodine isomer also produced by neutron capture in ^{129}I . In contrast, 25-min ^{128}I which is formed by neutron capture in

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