pose an ionic structure for the solid, and the behavior in halogen fluoride solutions is also indicative of the presence of ionic species. Electromigration and coprecipitation experiments are now being planned to determine the charge and chemical characteristics of the oxidized species. It is probable that stable solutions of radon in one or more positive valence states can be prepared in other nonaqueous solvents, such as hydrogen fluoride, antimony pentafluoride, or various metal hexafluorides.

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Spectroscopic Observation of the Triplet Excited State of Uracil in Solution

Sir:

Considerable work has recently been published on the effect of ultraviolet irradiation on the basic pyrimidines and purines in DNA and RNA, and on DNA itself (for recent reviews see ref 1–3). Various studies,[1-5] including photosensitization studies, have shown that dimerization of thymine and uracil occurs primarily from an excited triplet level, while an excited singlet state has also been invoked as the precursor under certain experimental conditions. Low-temperature (ethylene glycol–water glasses at 77°K) phosphorescence spectra of various nucleotides and dinucleotides have been observed,[1] but no triplet–triplet absorption spectra have been reported. Attempts[6] to determine triplet absorption spectra on flash photolysis of aqueous solutions of uracil, 5-bromouracil, and thymine at 20° were negative, using flash-duration resolution of $\sim$20 μsec. Such a failure was accounted as due to the short lifetimes of these triplets (estimated as 0.5–5.0 μsec) and the relatively low quantum yield.

A different approach to produce and study such triplets is presented here, using the much higher time-resolution available in the pulse radiolysis technique. The radiolysis of organic liquids is known to produce excited singlets and triplets which can transfer their energy to solutes. Naphthalene (N) and anthracene (A) triplets have, for example, been observed[7] on pulse radiolysis of solutions of N and A in various polar protic and aprotic solvents. Figure 1 shows the transient optical absorption spectra produced on pulse radiolysis of uracil in acetonitrile (AN), dimethylformamide (DMF), and isopropyl alcohol (i-PrOH). Single pulses of 2.3-MeV electrons, 30-nsec duration, were used;[8] the monitoring light entered a double monochromator and an EMI 9558 QB photomultiplier was employed.

The following observations and considerations support the assignment of this transient spectrum to the

(1) J. Eisinger and R. G. Shulman, Science, 161, 1311 (1968).
(2) J. G. Burr, Advan. Photochem., 6, 193 (1968).
(3) Papers presented at Symposium on "Basic Mechanisms in Photochemistry and Photobiology," Photochem. Photobiol., 7, 511 (1968).
(4) A. A. Lamola and J. P. Mittal, Science, 154, 1560 (1966).
(5) I. H. Brown and H. E. Johns, Photochem. Photobiol., 8, 273 (1968).
(6) (a) R. M. Danziger, E. Hayon, and M. E. Langmuir, J. Phys. Chem., 72, 3842 (1968); (b) M. E. Langmuir and E. Hayon, J. Chem. Phys., in press.
(7) E. Hayon, in preparation.
(8) For experimental details see (a) M. Simic, P. Neta, and E. Hayon, J. Phys. Chem., in press; (b) E. Hayon, J. Chem. Phys., in press.

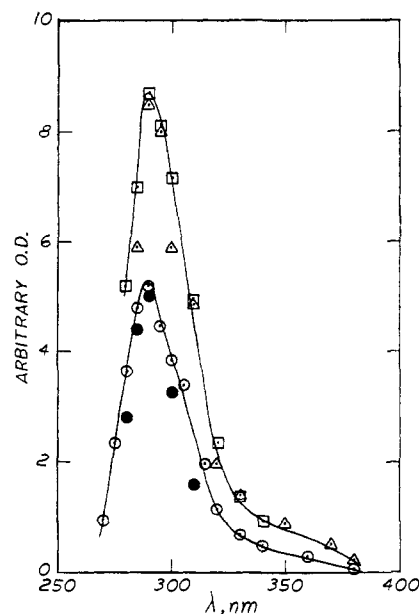Figure 1. Transient optical spectra obtained on pulse radiolysis of oxygen-free solutions of uracil in acetonitrile ($\odot$, 2×10^{-4} M), in dimethylformamide ($\square$, 7×10^{-4} M), and in isopropyl alcohol ($\triangle$, 2×10^{-4} M). The OD was measured at $\angle 0.2$ μsec after a 30-nsec pulse of electrons, dose per pulse $\sim$28 krads. Filled circles ($\bullet$) obtained from flash photolysis of oxygen-free 2×10^{-5} M uracil in acetonitrile, OD normalized to pulse data.

T–T absorption of uracil. (1) An identical transient absorption with λ_{max} 289 $\pm$ 1 nm has been obtained in the pulse radiolysis of uracil in five different organic liquids. (2) The amount of transient observed is directly proportional to the G value of N^T or A^T produced[7] in that solvent; e.g., G_{N^T} is 0.11, 0.19, and 0.20 in AN, DMF, and i-PrOH, respectively. (3) The flash photolysis[9] of 2×10^{-5} M uracil in AN and 1×10^{-5} M uracil in water at pH 5.0 in carefully degassed solutions is found to produce a similar spectrum with λ_{max} $\sim$290 nm (see Figure 1). (4) The transient is not due to an electron adduct of uracil since it differs from the absorption spectrum of such an adduct[8b] and is formed in N_2O-saturated solutions; furthermore, the extent of its formation does not correlate with the $G_{e^-_{solv}}$ produced[7] in these solvents. $G_{e^-_{solv}}$ is 0.44, 1.62, and 0.92 in AN, DMF, and i-PrOH, respectively. (5) The transient decays by a first-order process in the three solvents with a half-life, $t_{1/2} = 0.693/k$, of 6.0 $\pm$ 0.4, 10.0 $\pm$ 1.0, and 5.0 $\pm$ 1.0 μsec in AN, DMF, and i-PrOH, respectively, under the particular experimental conditions and uracil concentrations. (6) The absorption maxima of other pyrimidines and purines examined are shifted to higher or lower wavelengths; e.g., thymine triplet has λ_{max} $\sim$300 nm. (7) Taking[10] the T–T extinction coefficient of naphthalene as 22,600 M^{-1} cm^{-1}, the T–T extinction coefficient of uracil at 289 nm is determined to be $\geq$91,000 M^{-1} cm^{-1} ($\pm$10%), assuming equal formation of triplet states.

Full details on the nature of triplet excited states of various pyrimidines, purines, and dinucleotides and the effect of solute concentration, pH, O_2, and energy-trans-

(9) The flash photolysis set-up is described in ref 6a. The amount of transient produced under stated conditions was small, OD $\leq$ 0.01.
(10) E. J. Land, Proc. Roy. Soc. (London), A305, 457 (1968).

fer processes in mixtures of pyrimidines and purines will be published.

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Oxidation of Sulfides with t-Butyl Hypochlorite. Evidence for a Tetracovalent Sulfur Intermediate[1]

Sir:

t-Butyl hypochlorite is an excellent reagent for the oxidation of sulfides to sulfoxides without concomitant formation of sulfones.[2] In certain cases, interesting and synthetically useful stereochemical control of such oxidations is possible.[3] It has been proposed that alkoxysulfonium salts intervene in these oxidations;[2] such salts have been isolated after the addition of halide traps such as antimony pentachloride, mercuric chloride, or certain silver salts.[4] Several papers have already appeared with mechanistic suggestions concerning such reactions.[5] We now wish to report convincing evidence for the intervention of tetravalent sulfur species in such oxidations; we believe Scheme I describes the essential features of these reactions.

Scheme I
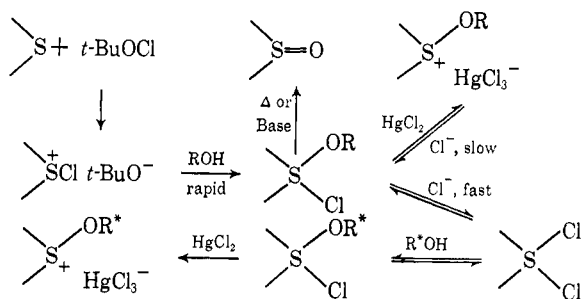
The hypochlorite oxidations are conducted at $-78°$. To thiane in methylene chloride was added 2 equiv of t-butyl hypochlorite followed by 1 equiv of mercuric chloride. Addition of ethyl ether caused the precipitation of the relatively unstable salt **1** (R = t-C₄H₉). The solid was rapidly analyzed by ir spectroscopy. A spectrum characteristic of a t-butoxy-sulfonium trichloromercurate was obtained. If ethanol (as little as 1 or 2 equiv) is present at the time of addition of the hypochlorite the principal product is salt **1** (R = C₂H₅). On the other hand, if the ethanol is added after the addition of the t-butyl hypochlorite the salt obtained upon addition of mercuric chloride is again the t-butyl salt. The reaction of t-butyl hypochlorite in ethanol is much faster than the reaction of ethyl hypochlorite; therefore, we are confident that, in the former case, ethyl hypochlorite is not the effective reagent. These results led to the suggestion that the chlorosulfonium salt **2** is the first intermediate

along the reaction coordinate and that this chloro-sulfonium salt reacts quickly even at $-78°$ to give an alkoxy intermediate. This alkoxy intermediate could be an alkoxysulfonium chloride (which may or may not exist as a tight ion pair)[6] or it could be a tetracovalent sulfur species. The evidence outlined below indicates the latter to be correct.
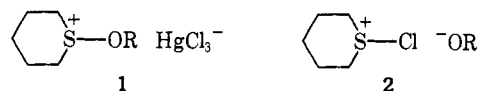
When alkoxysulfonium fluoroborates or trichloromercurates are dissolved in ethanol-1-^{14}C, the rate of exchange is quite slow (less than 5% per hour) even at room temperature. However, when trace amounts of hydrogen chloride (added as a saturated solution in methylene chloride) are added, alkoxy exchange is rapid and statistical (based on total available alkoxy groups in the reaction system). Thiane was allowed to react with t-butyl hypochlorite in ethanol at $-78°$ and the reaction mixture allowed to warm to room temperature over a 30-min period, followed by the addition of ethanol-1-^{14}C. The mixture then was allowed to stir for an additional 30 min at room temperature. Mercuric chloride was added; 1-ethoxy-thioniacyclohexane trichloromercurate (**1**, R = C₂H₅) was obtained at high yield and found to contain negligible radiolabel. These experiments indicate that the intermediate produced by the reaction of t-butyl hypochlorite and sulfide in alcohols has a relatively long lifetime even at room temperature and does not undergo rapid alkoxy interchange.

When the above reaction sequence was repeated, but with the addition of a catalytic amount of dry hydrogen chloride at the time of addition of the labeled ethanol, scrambling of the ethoxy group was found to be statistical after 15 min at room temperature. On the other hand, sulfuric acid does not catalyze the exchange, suggesting that catalysis is due to chloride ion rather than the acidity of hydrogen chloride. Salts such as tetra-n-butylammonium chloride are also effective catalysts. Apparently the trichloromercurate ion is not an effective source of halide ion under these conditions. Hydrogen chloride does not catalyze the exchange at $-78°$.

The observation that catalytic amounts of chloride ion catalyze exchange of alkoxysulfonium salts, coupled with the fact that the intermediate seems to be stable in the absence of chloride ion, leads to the suggestion that attack of chloride ion on the salt may be slow compared to subsequent steps leading to alkoxy interchange. If this were not true, small amounts of chloride ion would be rapidly consumed by the formation of the stable tetravalent intermediate and hence chloride ion in small amounts would not be an effective catalyst for statistical alkoxy exchange.

The nmr spectrum of the product of the reaction of methyl phenyl sulfide and t-butyl hypochlorite differs significantly from the spectrum of methylphenyl-t-butoxysulfonium fluoroborate. We do not anticipate that such differences could be entirely accounted for by ion-pairing phenomena and suggest that the data summarized in Table I provide additional evidence for a

(1) Part XX in the series Chemistry of Sulfoxides and Related Compounds. We gratefully acknowledge support by the National Science Foundation (Grant GP-8648).

(2) P. S. Skell and M. F. Epstein, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 26N

(3) C. R. Johnson and D. McCants, Jr., *J. Amer. Chem. Soc.*, **87**, 1109 (1965).

(4) C. R. Johnson and M. P. Jones, *J. Org. Chem.*, **32**, 2014 (1967).

(5) C. Walling and M. J. Mitz, *ibid.*, **32**, 1286 (1967); L. Skattebøl, B. Boulette, and S. Solomon, *ibid.*, **32**, 3111 (1967).

(6) For a recent discussion of tetracovalent sulfur intermediates and related ion pairs see H. Kwart, E. N. Givens, and C. J. Collins, *J. Amer. Chem. Soc.*, **90**, 7162 (1968).