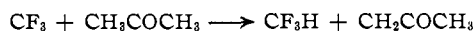relates well with the small amount of available data which indicates a non-variance in the activation energy for H-abstraction from a substrate by a perfluoroalkyl radical.[6,7] The activation energy for the reaction

$$CF_3 + CH_3COCH_3 \longrightarrow CF_3H + CH_2COCH_3$$

is 6.9 ± 0.1 kcal./mole,[3] assuming $E = 0$ for CF_3 radical recombination.

Discussion

Other values of cross-combination ratios involving simple alkyl and perfluoroalkyl radicals are unreliable, primarily because the measurement of the ratio was not the object of the experiments. From the work of Giacometti and Steacie[5] on the reaction between C_3F_7 and C_2H_6, ratios for C_3F_7 and C_2H_5 radicals varying from 1.99 to 4.31 may be obtained (previously quoted[1] as 3.2), scattered over the temperature range 360 to 469°K. The quantities of n-butane obtained in these experiments were extremely small compared to the other products, amounts varying from 1.8×10^{-9} to 6×10^{-11} mole/cc., which renders the cross-combination values very inaccurate, and, as previously noted, the analysis further suffered from lack of precision in the separation of $C_3F_7C_2H_5$ and C_6F_{14}.[12]

In a similar system involving the reaction of C_2F_5 radicals with CH_4, Price and Kutschke[10] find that in the majority of their experiments a cross-combination ratio for C_2F_5 and CH_3 radicals of approximately 2 ± 1 is obtained. The range of values is from 0.6 up to 6.77, over the temperature range 423 to 545°K.; again the quantities of ethane obtained, 2.0×10^{-9}

to 2.5×10^{-10} mole/cc., are very much less than the other products involved in the cross-combination ratio.

An interpretation of the pre-exponential ratio $A_{ab}/(A_{aa}A_{bb})^{1/2}$ obtained in this work is not obvious, and no theoretical relationship is expected if the steric factor for the sum of mutual disproportionation plus combination for some radical species is much less than unity.[20] The ratio of the collision numbers $Z_{ab}/(Z_{aa}Z_{bb})^{1/2} = 2.97$, using values for the collision diameters of $\sigma_{CH_3} = 3.5$ Å., $\sigma_{CF_3} = 4.0$ Å. and $\sigma_{C_3F_7} = 6.5$ Å. This gives the ratio of the steric factors, $P_{ab}/(P_{aa}P_{bb})^{1/2} = 0.743/2.97 = 0.25$. There is no a $priori$ reason to expect a steric factor of unity for the reaction between two C_3F_7 radicals, especially since disproportionation does not occur.

A previous attempt[21] to use the pre-exponential ratio obtained in the $CF_3 + CH_3$ system as a test of transition state theory is incorrect, as an erroneous value was used for the entropy of C_2F_6 at 298.16°K. and 1 atm. Better values[22] are 79.18 and 79.06 cal. deg.$^{-1}$ mole^{-1}; use of these values does not lead to any correspondence between the experimental and theoretical A-factor ratios.

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(21) G. O. Pritchard, H. O. Pritchard, G. H. Miller and J. R. Dacey, *ibid.*, **38**, 319 (1960).

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Some Observations Related to the Photoreduction of Chlorophyll[1]

By Robert Livingston and P. J. McCartin[2]

The efficiency of quenching of the triplet state of chlorophyll a by ascorbic acid in pyridine increases with the water content of the solvent. The bimolecular quenching constant is approximately 10^4 M^{-1} sec.$^{-1}$ for dry pyridine, but increases to about 1.5×10^5 M^{-1} sec.$^{-1}$ for pyridine containing 25% water. The quenching of the triplet is accompanied by the formation of a labile intermediate, whose absorption spectrum has a maximum near 480 mμ. Under our experimental conditions, the decay of this intermediate was first order, with a half-life of about 10 msec. The product of this decay appears to be, in part, Krasnovsky's pink pigment.

Introduction

Recent studies demonstrate that the photoreduction of chlorophyll occurs by way of the triplet state,[3-6] that the efficiency of the reaction depends upon the water content of the solvent when ascorbic acid is the reductant,[4-7] and that the formation of the pink, fully-reduced chlorophyll is preceded by one or more intermediates.[4-6,8] The present work consists of an experimental re-examination of some of these findings.

Materials.—Reagent grade pyridine was used. It was dried by distilling over CaH_2 and then degassing in the presence of

CaH_2. Ascorbic acid was either Mallinckrodt, USP or Eastman, White Label, used as supplied. In a few experiments, it was crystallized from water and dried by evacuaton. The dehydroascorbic acid, a Nutritional Biochemicals Corp. product, was used without further purification. The methods of preparation and purification of chlorophyll a have been described elsewhere.[9]

Preparation of Solutions.—All solutions were deoxygenated by four or more cycles of freezing, pumping, thawing, freezing, etc. The pumping reduced the pressure to a "black vacuum" ($\leqslant 10^{-6}$ mm.), while the solution was at a liquid nitrogen temperature. In preparing solutions containing ascorbic acid, a weighed sample of the crystalline acid and a known volume of pyridine were evacuated in separate vessels which were attached to the same vacuum manifold. After the solvent had been deoxygenated, it was distilled into the vessel containing the solid, and the resulting solution was again subjected to successive freezing, pumping and thawing. Preliminary experiments had demonstrated that even exhaustive pumping did not effectively remove the O_2 dissolved in the crystalline solid. In all experiments, the concentration of chlorophyll a was 5×10^{-6} M.

Apparatus.—The flash-photolytic apparatus has been described elsewhere.[10] The scanning light was rendered approximately monochromatic by means of second-order interference filters.

(1) This investigation was supported by a PHS research grant (A-2733) from the Division of Arthritis and Metabolic Diseases of the U. S. Public Health Service.

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(3) V. B. Evstigneev, V. A. Gavrilova and A. A. Krasnovsky, *Doklady Akad. Nauk*, **74**, 315 (1950).

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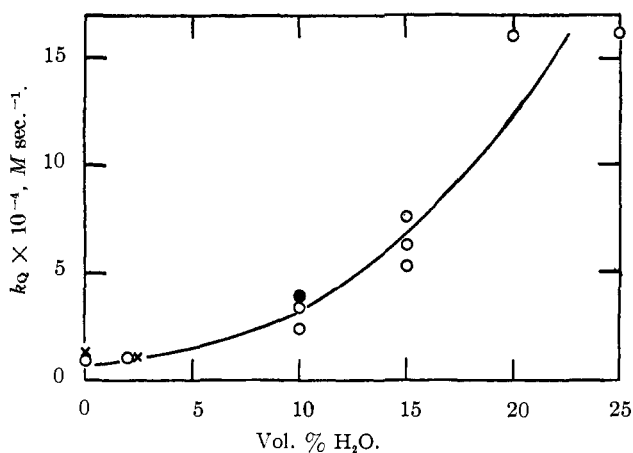
Fig. 1.—The bimolecular quenching constant as a function of the water content of the solvent; pigment, chlorophyll a, 5 × $10^{-1} M$; quencher: O, ascorbic acid, 0.010 M; ●, ascorbic acid, 0.050 M; ×, phenylhydrazine, 0.080 M.

Results

Quenching of the Triplet State.—The data of Fig. 1 demonstrate that the quenching of the triplet state of chlorophyll by 0.010 M ascorbic acid is barely detectable when the solvent is dry pyridine, but becomes increasingly efficient when the water content of the solvent is increased. Ascorbic acid is a weak quencher, at best; its bimolecular quenching constant, k_Q, is about one hundred thousandth fold as large as the corresponding constants for O_2 or quinone.[6,11] The values of k_Q are least reliable at the highest and lowest concentrations of water. In the presence of a high concentration of water, rapid photochemical degradation of chlorophyll[7] makes it impossible to repeat measurements with the same solution. At low concentrations of water, the quenching is slow relative to the spontaneous decay $(k_1 \cong 800 \text{ sec.}^{-1})$[6b,11,12] and the uncertainty of k_Q probably approaches ±100%.

The present values of k_Q are about one-tenth as large as the preliminary values reported by Livingston and Pugh.[4] Although the source of this discrepancy cannot be established definitely, it is probably the result of our more careful removal of O_2 from the solid ascorbic acid. An impurity of 0.01 mole per cent of O_2 in the ascorbic acid could be responsible for a tenfold increase in the apparent value of k_Q for ascorbic acid. The possibility that the observed quenching was due in all or in part to dehydroascorbic acid present as a contaminant of ascorbic acid, was tested directly by adding dehydroascorbic acid to a solution of chlorophyll in pyridine. Even at the moderately high concentration of 5 × 10^{-3} M, no quenching was observed.

A few measurements were made using 0.080 M phenylhydrazine as a quencher. The results of these measurements indicate values of k_Q of 1.3 × 10^4 and 1.1 × 10^4 M^{-1} sec.$^{-1}$ for phenylhydrazine in dry and wet (2.4% H_2O) pyridine, respectively.

The Long-lived Intermediate.—We have confirmed the earlier observations[4,5] of the occurrence of a moderately long-lived intermediate, having an absorption maximum near 470 mμ. When aqueous pyridine solutions of chlorophyll and ascorbic acid are flashed, the relatively rapid disappearance of the triplet is followed by a much slower decay of a transient absorption. This effect is marked at 460 and 480 mμ, but is not detectable at 500 or 550 mμ. At 525 mμ, instead of

the disappearance of a transient absorption, a slow increase in absorption was observed, the increase being permanent on our time scale. This increase at 525 is almost certainly due to the formation of Krasnovsky's pink pigment.[5] The results at the other wave lengths indicate that neither the intermediate nor the pink pigment absorb appreciably at 550 mμ, that the intermediate and the pink pigment have an isosbestic point near 500 mμ, and that the absorption of the intermediate is greater than that of the pink pigment at 480 and 460 mμ. These conclusions are in agreement with Zieger and Witt's[5] more detailed determination of the absorption spectra.

Under our experimental conditions, the decay of the intermediate conformed to a first-order law; no second-order term was detectable. Although the variation of the half-life was greater than the apparent random errors of the measurements, the half-life appears to be independent of the water content of the solvent.

H_2O, %	<0.1	3.7	10	10	15	25
$\tau_{1/2}$, msec.	12	14	10	18	14	11

The above results were obtained with 0.010 M ascorbic acid solutions. One measurement, made with 0.0010 M ascorbic acid in pyridine containing 40% H_2O, yielded a value of 8 msec. When phenylhydrazine was used as the reductant, half-lives of 7 and 12 msec. were observed in dry and wet pyridine, respectively. One solution, containing 10% H_2O and 0.010 M ascorbic acid, was flashed at 23° and −40°. Within the limits of random error (±1.0 msec.) the half-life was 10.0 msec., independent of temperature.
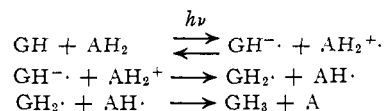
In all of these (preceding) measurements, the wave length of the scanning light was approximately 480 mμ. Two measurements made with 525 mμ (0.010 M ascorbic acid and 10% H_2O) indicated an increase in optical density, due to a first-order process with a half-time of about 25 msec.

No long-lived intermediate was formed when chlorophyll was flashed in wet or dry pyridine which contained neither ascorbic acid nor phenylhydrazine.
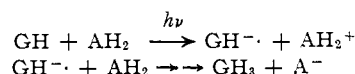
Discussion

Both Livingston and Pugh[4] and Zieger and Witt[5] suggest that the intermediate with an absorption maximum at 480 mμ is probably the same as one of the electrode-active intermediates observed by Evstigneev and Gavrilova.[8,13] There are, however, certain difficulties which must be met in making this identification. The Russian writers report that the electrode effect persists for seconds after the termination of the illumination and that at −40° the absorption at 525 mμ increased for 8 or 9 minutes in the dark. These changes appear to be much slower than those which have been observed in the flash-photolytic experiments.
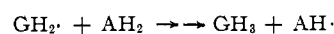
Furthermore, if one accepts Krasnovsky's mechanism[6a] for the formation of the pink pigment, GH_3,

$$GH + AH_2 \underset{}{\overset{h\nu}{\rightleftarrows}} GH^- \cdot + AH_2^+ \cdot$$
$$GH^- \cdot + AH_2^+ \longrightarrow GH_2 \cdot + AH \cdot$$
$$GH_2 \cdot + AH \cdot \longrightarrow GH_3 + A$$

the disappearance of either $GH^- \cdot$ or $GH_2 \cdot$ should be a second-order reaction. The mechanism may be modified to conform to a first-order decay of the intermediate, as

$$GH + AH_2 \overset{h\nu}{\longrightarrow} GH^- \cdot + AH_2^+$$
$$GH^- \cdot + AH_2 \rightarrow \rightarrow GH_3 + A^-$$

or

$$GH_2 \cdot + AH_2 \rightarrow \rightarrow GH_3 + AH \cdot$$

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(13) V. B. Evstigneev and V. A. Gavrilova, *Doklady Akad. Nauk*, **95**, 841 (1954).

followed by

$$2AH\cdot \longrightarrow AH_2 + A, \text{ etc.}$$

However, this type of mechanism is consistent with a first-order decay only if all of the intermediate disappeared by forming the pink pigment, which is not consistent with the estimated quantum yields of formation. At moderately high concentrations of water and ascorbic acid, the efficient quenching of the triplet indicates a quantum yield of formation of the intermediate of the order of magnitude of unity, much greater than the observed yield[7] of the pink pigment.

It appears probable, therefore, that under our experimental conditions the intermediate disappears

$$GH_2\cdot (\text{or } GH^-) + Ox. \longrightarrow \longrightarrow GH + Red.$$
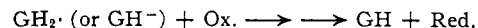
chiefly by reacting with an adventitious oxidant. If the concentration of the oxidant were much greater than that of the intermediate, its rate of decay would be first order, but not if the concentrations were of the same order of magnitude. This condition excludes the possibility that O_2 is the oxidant; since the observed, spontaneous rate of decay of the triplet was normal, indicating an O_2 concentration less than 5×10^{-7} M. It is probable that our samples of ascorbic acid were appreciably contaminated with dehydro-ascorbic acid and that it acted as the oxidant (compare ref. 3, p. 302). Additional experiments should be performed to test these suggestions.

The Structure of the Nuclear Magnetic Resonance Lines for Methane Adsorbed on Rutile

BY J. G. ASTON AND H. W. BERNARD

RECEIVED JULY 30, 1962

A study of the temperature dependence of the nuclear magnetic resonance line characteristics has been made for solid methane and for methane adsorbed on titanium dioxide. This confirms previous conclusions that the line narrowing is due to diffusion processes. Reasons are given for concluding that the data give no information about the rotational process that sets in at the lambda point. The presence of the line of intermediate width well below the lambda point and the appearance of the narrow line only at temperatures well above the lambda point are the only differences from the behavior of carbon tetrafluoride and neither of these is directly connected with the onset of rotation.

I. Introduction

The original nuclear magnetic resonance data of Alpert[1] was at first taken to indicate that the lambda point in methane was not a transition involving rotation or re-orientation. However, Eucken and Veith[2] had previously made a study of the low temperature heat capacities of solutions of krypton in solid methane from below to well above the lambda point from which they had concluded that a rotational transition occurred at the lambda point. A careful analysis of their data indicates that almost completely free rotation exists above the transition.[3]

This investigation was performed in an effort to investigate further the motions in solid methane by a comparison of the behavior of the nuclear magnetic adsorption line of the solid with that when methane is adsorbed on heterogeneous surfaces of high area[4,5] as was done for carbon tetrafluoride.[6,7]

Proton resonance derivative line shapes have therefore been obtained for methane adsorbed on high surface area titanium dioxide at various coverages from 0.33 to 8.06 layers, and also in bulk methane, as a function of temperature. The results are compared with the corresponding ones for carbon tetrafluoride.

II. Experimental

Apparatus.—Details of the apparatus, cryostat, precise method of temperature control,[8] titanium dioxide sample and drying procedure have been described elsewhere.[7]

In the studies on bulk methane the titanium dioxide was omitted from the sample holder in one set of measurements.

The Methane Sample.—The sample contained less than 0.2 mole % impurity as deduced by mass spectrograph analysis.

Line Widths.—The method of recording the derivative of the adsorption has been described.[9] Where a line was considered to consist of two components, curves were arbitrarily drawn so as to add up to the observed curve and each component was treated separately. Figure 1 shows a typical line shape derivative curve. Second moments were obtained from the derivative curves in the usual way.[9]

III. Results

A graph of line width against temperature for bulk methane in the presence of titanium dioxide and without titanium dioxide is given in Fig. 2. Measurements were made on bulk methane after removing the titanium dioxide from the sample container to ascertain the effect of titanium dioxide. The only difference was the absence of the narrow components below 70°K.

A narrow line of approximately one gauss persists down to about 54°K. for bulk methane in the presence of titanium dioxide. On warming, the broad line begins to narrow at about 60°K. No narrow line component was detected below 54°K. as was reported by Fuschillo and Renton[10] of results obtained in this Laboratory. The broad line component was found to be a little more than 6 gauss wide at its maximum, with and without titanium dioxide, which is about 2 gauss less than that reported by Thomas, Alpert and Torrey,[11] but is in agreement with that found by Fuschillo and Renton. While we speak of this as the broad line, it is actually one of intermediate width in terms of the carbon tetrafluoride results.[9] There is no really broad line observed analogous to that observed for carbon tetrafluoride.

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