resolution by the gas chromatography column used. In most cases the structure of the C_5 and C_6 iodides was not determined; however, from the position of these products on the gas chromatogram an indication of the structure could be obtained. *t*-Butyl iodide could not be determined because of its easy decomposition at elevated temperatures. In all cases, 2,2-dimethylbutane a possible exception, the presence of iodine eliminated both the C_i and C_d products. The effect of iodine on the C_1 products is less certain because of volatility losses. It was noted, however, that iodine decreased the methane yield from 2,2-dimethylbutane by only one-half.

The iodide products from *n*-hexane consisted mainly of the *n*-alkyl type with the exception of the C_6 iodide which was 20% *n*-hexyl and 80% *sec*-hexyl. In general the iodide products from the branched isomers, apart from methyl and ethyl iodide, did not contain any appreciable quantities of *n*-alkyl iodides. The total alkyl iodide yield from the hexanes was approximately the same as that reported for liquid butane.[5]

A surprisingly large yield of ethyl iodide was obtained from 2-methylpentane while only a negligible amount of C_4 iodide was observed. The C_3 iodide was entirely isopropyl showing that a simple C–C bond fission at the branch site does not occur since this would lead to equal amounts of isopropyl and *n*-propyl iodides. The distribution of alkyl iodide products from 3-methylpentane was in qualitative accord with the C_i product distribution shown in Table IV. The C_4 iodide product was entirely *sec*-butyl. The non-equivalence of the methyl iodide and pentyl iodide yields again showed that simple C–C bond fission into radicals does not occur.

Conclusion.—The products observed from the branched alkanes show, in most cases, a preference for C–C bond fission at points adjacent to the branch site. Qualitatively, similar behavior can be seen in the mass spectral fragmentation patterns. However, two important differences should be noted. The mass spectra of 3-methylpentane and 2,2-dimethylbutane show very large rearrangement peaks. There was no evidence that such rearrangement processes were important for the radiolysis of the liquids. It may well be that this kind of rearrangement process is quenched in the condensed phase but might be observed in vapor phase radiolysis. The second important difference was noted in the abundance of the parent fragment. The parent ion peaks in the mass spectra of the branched hydrocarbons are exceedingly small whereas in the liquid radiolysis the parent fragment is a major component of the total product observed. This difference undoubtedly reflects the effect of state on the abundance of the parent fragment.

The observed non-equivalence of radical fragments in many cases suggests that simple C–C bond fission does not occur. It is evident that conventional free radical chemistry does not apply insofar as the fragmentation processes are concerned. It may be that ion-molecule reactions, which could generate free radicals in non-equivlaent amounts, play an important role even in the condensed phase. Similar reactions involving the interaction of excited molecules could also be written to give a non-equivalence of radicals.

Acknowledgments.—The author is indebted to J. S. Balwit for the irradiations and to the Analytical Unit for the infrared measurements.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY, UNIVERSITY OF MINNESOTA, INSTITUTE OF TECHNOLOGY]

Some Properties of the Ground Triplet State of Chlorophyll and Related Compounds[1]

BY ROBERT LIVINGSTON AND EIJI FUJIMORI

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The absorption spectra of the lowest triplet states of certain polyatomic molecules were measured by the use of the flash photolytic-flash photographic technic. The compounds studied included chlorophylls-*a* and -*b*, pheophytins-*a* and -*b*, Zn-chlorophyll-*a*, several porphyrins and Mg-phthalocyanine. In general, these spectra resemble those which have been published for the triplet states of the chlorophylls. The principal absorption maxima of the ground state do not appear in the absorption of the triplet state and are replaced by a broad absorption, having a maximum on the long wave length side of the Soret band and gradually decreasing toward the red. No transients were detectable for copper or iron substituted porphyrins or for Cu-chlorophyll-*a*, presumably due to the short lives of the triplet states of these molecules.

A long-lived excited state, presumably the lowest triplet state, plays an important role[2a] in the photochemical reactions of dyes and pigments. The development of the flash photolytic technique[2b] has made possible the direct study of some properties of the triplet states of these molecules. The present results were obtained with a flash-photolytic, flash-spectrographic apparatus, patterned on that of Porter and Windsor.[3] While this method is well adapted to the measurement of the wave lengths of absorption maxima, it yields only semi-quantitative values of the extinction coefficients of broad, relatively structureless absorption curves which are characteristic of the triplets of chlorins and porphyrins. A few qualitative observations of the half-lives of certain compounds are included in this report. The results of detailed kinetic studies of the decay of the chlorophyll triplet, which were ob-

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[1] This work was supported by a grant from the National Science Foundation (NSF-G 1449) for which the authors are grateful.

[2] (a) E. Rabinowitch, "Photosynthesis," Interscience Publishers, New York, N. Y., pp. 484–547 and 1507–1528; (b) G. Porter, *Proc. Roy. Soc.* (*London*), **A200**, 284 (1950).

[3] G. Porter and M. Windsor, *Disc. Faraday Soc.*, **17**, 178 (1954).

TABLE I

ABSORPTION MAXIMA CORRESPONDING TO THE TRIPLET STATES

Compound	Solvent	Conversion, %	Abs. max.,[a] $m\mu$	Range of λ's studied, $m\mu$
Chlorophyll-*a*	Benzene (wet)	85	(440?), 465	410–750
Chlorophyll-*a*	Benzene (dry)	60	450?	410–750
Chlorophyll-*a*	Methanol	80	450, (550?)	420–660
Chlorophyll-*a*	Pyridine	85	460	380–740
Chlorophyll-*a*	Pyridine	95	(370), 462, (530)[b]	380–740
Chlorophyll-*b*	Benzene (wet)	80	430?, 480	420–680
Chlorophyll-*b*	Benzene (dry)	65	440?, 475, (580?)	420–690
Chlorophyll-*b*	Pyridine	90	480	380–740
Chlorophyll-*b*	Pyridine	90	(445), 485, (550) (605)[b]	380–730
Pheophytin-*a*	Benzene (wet)	75	430?, 500	420–690
Pheophytin-*a*	Pyridine	75	430?	420–690
Pheophytin-*b*	Benzene (wet)	75	430?, 460, (510)	420–690
Pheophytin-*b*	Pyridine	75	410?, 460, (520?)	380–690
Zn-Chlorophyll-*a*	Benzene (wet)	70	450	420–750
Zn-Protoporphyrin	Methanol	75	455	430–670
Protoporphyrin	Methanol	60	440, (530?)	430–680
Protoporphyrin	Pyridine	60	350, 420	350–680
Mesoporphyrin	Pyridine	60	450	440–680
Tetraphenylchlorin	Benzene (wet)	80	470, 520?	450–690
Mg-Phthalocyanine	Pyridine	65	400, 470	380–710

[a] Parentheses indicates that the wave lengths correspond to minor absorption bands; question marks, that the observed maxima are of doubtful significance. [b] Results of Linschitz and Sarkanen.[13]

tained by a different method, have been published elsewhere.[4]

Experimental Methods and Materials

Materials.—The methods of preparation and purification of chlorophylls *a* and *b* have been described elsewhere.[5] We are indebted to Dr. A. W. Frenkel for the sample of bacteriochlorophyll–protein complex; to Drs. R. Lumry and S. Takashima for the purified hemoglobin; to Dr. S. Schwartz for mesoporphyrin; and to the du Pont Corp. for the purified sample of magnesium phthalocyanine. The porphyrins were further purified chromatographically. The metallic derivatives of chlorophyll-*a*[7] and of the porphyrins[6,7] and the iron hemins[8] were prepared by standard methods. The solvents were high-grade commercial materials and, when it appeared necessary, were further purified by standard methods.[9]

Solutions.—All solutions were carefully deoxygenated. Except for the pigment–protein complexes, the pigments were added to the cuvettes as known volumes of standard solutions and the solvent was pumped-off on a vacuum line. The solvent which was used to prepare the final solution was in a separate receptacle, attached to the vacuum line. It was degassed, first, by boiling off about one quarter of it under vacuum, and, then, by successive freezing and evacuation, at liquid nitrogen temperatures, allowing it to melt under vacuum. By tilting a segment of the vacuum line, the required volume of the solvent was poured into the cuvette. The solution was then cooled and the cuvette sealed off under vacuum.

Apparatus.—Both the flash lamps and the cuvettes were made of Pyrex and were about 15 cm. long and 1.0 cm. inside diameter. In these lamps, Mallory elkonite electrodes were used; they completely eliminated the blackening, which is very troublesome when tungsten electrodes are used. Before filling, the lamps were thoroughly degassed at a temperature slightly below the softening point of Pyrex and with the electrodes raised to red heat by means of an induction furnace. They were filled with krypton at about 20 cm. pressure.

A 1 μF. condenser, raised to 10 kv., was discharged through each lamp. Spontaneous breakdown was prevented by a spark gap in series with the lamps. The triggering pulse was applied to the spark gap. The photolytic flash lamp was situated parallel to the cuvette, both being enclosed in a $BaSO_4$-lined box. The spectrographic flash was placed for end-on illumination of the cuvette. The light passing through the cuvette entered the slit of a Steinheil spectrograph. Glass optics were used in the spectrograph for measurements between λ4100 and 7600 Å. and quartz optics for the range λ3800 to 4300 Å. Eastman spectrographic plates (103-F (3), 103-O and 103-U) were used, depending upon the wave lengths being studied. The time, temperature and conditions of development were controlled carefully.

Procedure.—A number of spectra were recorded on each plate. With a solution-filled cuvette in place, several exposures were made separately with the spectrographic and photolytic flashes and with the photolytic flash followed, approximately 20 μsec. later, by the spectrographic flash. After replacing the solution with the solvent, the plate was exposed to the spectrographic flash though each of the steps of a Hilger rhodium-on-quartz stepped wedge.

The optical densities of the solutions were determined, at each wave length, by comparing the blackening of the plate for exposures through the solution to those obtained through the solvent and the several steps of the wedge. In some instances, it was necessary to correct[10] the blackening for the effect of scattered or fluorescent light.

The method of estimating the absorption curve for a transient from measurements of solutions containing mixtures of the transient and the normal compound has been discussed elsewhere.[11] Such analyses yield absorption curves whose forms appear to be, in general, reliable. The greatest uncertainties are in the determinations of the extinction coefficients where the optical densities are small. The extinction coefficients of the triplet states of chlorophyll and related molecules appear to be appreciable for all wave lengths studied.

Results

The technique, described in the preceding section has been applied to solutions of chlorophylls-*a*

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(8) *Org. Syntheses*, **21**, 53 (1941).

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(11) (a) E. Adams and L. Rosenstein, *ibid.*, **36**, 1452 (1914); (b) A. Hardy and F. Young, *J. Opt. Soc. Am.*, **38**, 854 (1948).

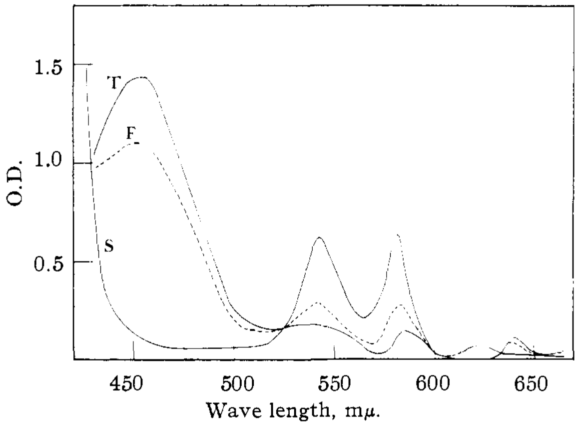

Fig. 1.—Absorption spectra of Zn-protoporphyrin: S, absorption spectrum of the ground state; F, absorption spectrum observed immediately after the photolytic flash; T, absorption spectrum estimated for the triplet state.

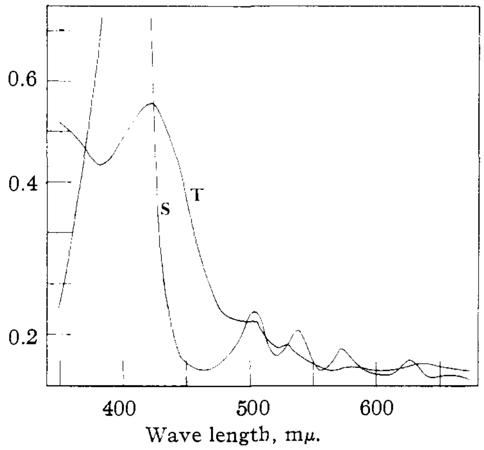

Fig. 2.—Absorption spectra for protoporphyrin: S, absorption spectrum of the ground state; T, absorption spectrum estimated for the triplet state.

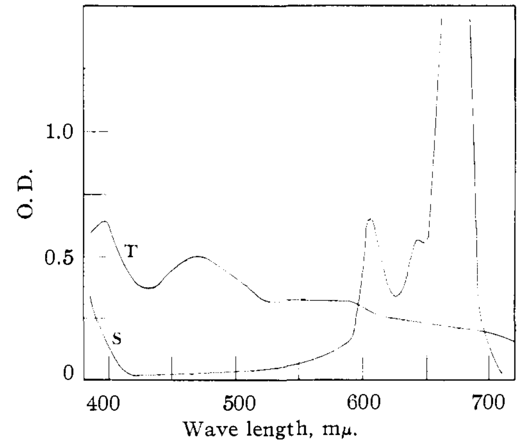

Fig. 3.—Absorption spectra for Mg-phthalocyanine: S, absorption spectrum of the ground state; T, absorption spectrum estimated for the triplet state.

and -*b* in wet and dry[12] benzene and pyridine and of chlorophyll-*a* in methanol. Subsequent to the completion of this work, Linschitz and Sarkanen[13] published absorption curves for the triplet states of chlorophylls *a* and *b* in pyridine. They used a photoelectric rather than a photographic method of determining the extinction coefficients and their data appear to be more reliable than ours. For chlorophyll-*b* (in pyridine) our values agree surprisingly well with theirs; the two curves are practically coincident at λ 380, from 490 to 540, and at 700 mμ. Between 550 and 680 our values are from 10 to 30% lower and between 400 and 480 mμ about 20% higher than theirs. The agreement for chlorophyll *a* solutions is less satisfactory; our values are apparently uniformly too high. However, the general forms of the curves for this compound are similar; the wave lengths for the principal maximum are in agreement and in both curves the relatively structureless absorption extends to wave lengths longer than 740 mμ, with no indication of a maximum in the red.

Essentially similar results were obtained in the other solvents. These data are summarized in Table I. It is noteworthy that the maximum per cent. of conversion to the triplet appears to be somewhat less in dry benzene than it is in the other solvents. Otherwise, there is no marked difference between the results obtained in dry and wet benzene.

In addition to the results for the chlorophylls Table I includes data for the pheophytins, Zn-chlorophyll-*a*, Zn-protoporphyrin, protoporphyrin, *meso*-porphyrin, tetraphenylchlorin and Mg-phthalocyanine. The absorption curves for three of these substances (Zn-protoporphyrin, protoporphyrin and Mg-phthalocyanine) are reproduced in Figs. 1, 2 and 3. In a general way, the absorption curves for the triplet states of all of these compounds resemble those of the chlorophylls. In each case there is a definite maximum lying to the long wave length side of the Soret band of the singlet and a broad, relatively smooth absorption curve extending into the red. The minor maxima of the zinc protoporphyrin curve are of doubtful significance but the maximum at 470 mμ on the Mg-phthalocyanine is almost certainly real.

Using the same apparatus and techniques which yielded the results listed in the preceding table, we were unable to detect any transient changes in the absorption spectra of the following (deaerated) solutions: Cu^{++}- and Fe^{++}- protoporphyrin in methanol, Fe^{+++}-protoporphyrin in either methanol or pyridine, Cu^{++}-chlorophyll-*a* in benzene, β-carotene in benzene, *p*-benzoquinone in benzene and *p*-nitroaniline in methanol.

The effect of Cu and Fe ions in eliminating the observable formation of flash induced transients of protoporphyrin and chlorophyll is of interest in relation to recent findings of Becker and Kasha.[14] These authors observed a strong phosphorescence of Cu- or Ni-complexed chlorophyll-*a* or etioporphyrin, dissolved in glassy media at liquid nitrogen temperatures. The presence of the paramagnetic ions quenches the fluorescence of these compounds but markedly increases the intensity of their phosphorescence. The authors conclude that the tran-

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(12) R. Livingston, W. Watson and J. McArdle, THIS JOURNAL, **71**, 1542 (1949).

(13) H. Linschitz and K. Sarkanen, *ibid.*, **80**, 4826 (1958).

(14) R. Becker and M. Kasha, *ibid.*, **77**, 3669 (1955).

sition from the first excited singlet to the ground triplet state

$$D^* \longrightarrow D'$$

is greatly enhanced by the paramagnetic ion. Presumably the probability of the radiative transition

$$D' \longrightarrow D + h\nu'$$

likewise is increased. The present results demonstrate that the non-radiative transition

$$D' \longrightarrow D$$

similarly is enhanced. At room temperature in fluid solvents, the non-radiative transition is dominant; but, at low temperatures in rigid solutions, the radiative transition (phosphorescence) is relatively important. The non-radiative process appears to be strongly dependent upon either the temperature or the viscosity of the medium, while the radiative transition is probably largely independent of these factors.

We were likewise unable to observe any transient spectral changes when aqueous solutions of hemoglobin, oxyhemoglobin or the bacteriochlorophyll–protein complex were used.

In an attempt to confirm Gibson's interesting results[15] we made a few measurements using carboxyhemoglobin in water, in the presence and in the absence of air. A flash of light induced in these solutions a short-lived increase in absorption at wave lengths between 400 and 455 mμ. The half duration of this transient was roughly 250 μsec. That this change was due to the same photochemical intermediates as were studied by Gibson is improbable; the present data are insufficient to resolve this doubt.

[15] Q. Gibson, *J. Physiol. (London)*, **134**, 123 (1956).

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Surface Tension of Synthetic High Polymer Solutions. II[1]

BY SUHAM AL-MADFAI AND H. L. FRISCH[2]

RECEIVED JUNE 6, 1958

The equilibrium value and the rate of approach to equilibrium of the surface tension of purified block copolymers of polyethylene oxide and polyoxypropylene in tetralin have been measured. As in the polystyrene–tetralin system,[3] the surface tension increment of relatively dilute solutions changes sign from minus to plus as the molecular weight of the polymer solute decreases. Further surface tension measurements are reported on a mixture of a high and low molecular weight polystyrene fraction in tetralin which have individually been studied[3] previously and on polyvinyl alcohol fractions in water (in particular one foam fractionated sample).

Introduction

In a previous communication[3] we described the use of a modified pendant drop apparatus for the investigation of the equilibrium value and the rate of approach to equilibrium of the surface tension (s.t.) of polymer solutions and reported s.t. data on a number of polystyrene (PSt) fractions in tetralin. The s.t. increment (*i.e.*, s.t. of the solution – s.t. of the solvent) of the PSt solutions changes sign as the molecular weight of the polymer solute decreases, as expected from theory,[4] due to an entropy effect. This in turn suggested[3] that s.t. measurements on a solution of polydisperse polymer sample may be sensitive to the low molecular weight tail of the molecular weight distribution.

We report here the results of s.t. measurements on tetralin solutions of purified block copolymers obtained by condensing ethylene oxide (EO) on a polyoxypropylene base (PO) to form polymers whose structure is believed to be HO-$(C_2H_4O)_x$-$(C_3H_6O)_y$-$(C_2H_4O)_z$-H (POEO).[5] Like the PSt–tetralin solutions,[3] the POEO–tetralin solution s.t. increments change sign (from minus to plus) as the molecular weight (M) of the polymer solute decreases. To test the sensitivity of a s.t. measurement to the presence of lower molecular weight polymer the s.t. of a mixture of two PSt fractions (M = 1.6 × 10^4, 8.7 × 10^4) in tetralin has been found.

Experimental

All s.t. measurements were carried out at 25 ± 0.1° using the pendant drop apparatus whose construction and operation were described elsewhere.[3]

Three POEO samples were studied; these were highly purified Pluronic (surfactant type) L31, L61 and L81[5] whose characteristics are listed

Sample	EO/PO ratio	*M* (Chem.)	Cloud pt., °C., 10% sol.	Ash content, %
POEO-L31	0.18	1070	29	0.01
POEO-L61	.15	2045	17	Nil
POEO-L81	.18	2470	15	Nil

The two PSt fractions and two polyvinyl alcohol (PVA) fractions used have been characterized previously.[3] One of the PVA fractions having a viscosity average degree of polymerization of 1700 was further foam fractionated. 250 ml. of a 1 g./100 ml. aqueous solution of this PVA was placed in a beaker and nitrogen was bubbled through the solution by means of a gas dispersing tube. The rate of flow of nitrogen was adjusted so that half of the polymer solution was foamed out over a period of about two hours. After all the foam had been removed, the remaining PVA solution was transferred to a weighed beaker and dried at 65 ± 10° to constant weight. The resultant PVA film was partially redissolved in water to a known volume of solution. The portion of the film remaining in the beaker was dried again to constant weight. A 0.804 g./100 ml. aqueous PVA solution was thus obtained having a viscosity number

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[1] Supported by the Office of Ordnance Research, U. S. Army.

[2] Address reprint requests to H. L. Frisch, Bell Telephone Laboratories, Murray Hill, N. J.

[3] H. L. Frisch and S. Al-Madfai, THIS JOURNAL, **80**, 3561 (1958).

[4] H. L. Frisch and R. Simha, *J. Chem. Phys.*, **27**, 702 (1957).

[5] We are indebted to Dr. D. R. Jackson and Dr. K. C. Frisch of the Research Department of the Wyandotte Chemical Corporation for supplying us with these purified polymers.