Fig. 5.—Electronegativities of nitrogen and phosphorous as a function of s character of the hybrid orbital. Solid line, nitrogen; broken line, phosphorus.

postulated. Computations of electronegativities of positive ions are now in progress, and it is hoped that values for partially charged atoms may also be obtained.[41] It was found in this Laboratory that these values are urgently required in order to get explanations[40] for hybrid and ionic character of chemical bonds consistent with n.q.r. frequency changes and other molecular properties.

(41) Note added in proof.—Such values have been obtained and are in the process of publication.

These subjects have been studied in a recent review article by Bent.[16] By considering compounds of the type X–A–Y, he has examined qualitatively the influence of the more electronegative group Y on the character of the bond X–A. He has attempted to explain the observed changes in the X–A bond, when going from X–A–X to X–A–Y by considering only rehybridization of atom A, combined with the postulate that the electronegativity of an orbital of A increases when its s character increases. The first conclusion, that A becomes more electronegative in its bond to X is reasonable. But, the second conclusion drawn, that this is only due to increased s character in the bonding orbital of A toward X, appears dubious. As Coulson[42] has shown, the bond strength is not only governed by the overlap, but also by the energy match of the bonding orbitals; e.g. the bond is stronger, the better the energies match. If this concept is applied in Bent's picture, it is easily seen that increasing the s character of the A orbital toward X upsets the energy match of A with X, and also a corresponding increase of p character in the orbital toward Y makes the energy mismatch larger. But, if we consider, in addition to rehybridization, partial charges on the atoms, all the examples presented can be explained, and the energy match will be found to improve.

Thus, it must be pointed out that the picture given by Bent is questionable, since for simplicity's sake he has chosen not to introduce partial charges which is a serious approximation in a valence bond treatment. In order to make a more complete study possible, it is necessary to examine thoroughly the dependence of the orbital electronegativities on partial charges on the atoms.

(42) C. A. Coulson, Proc. Phil. Soc., 33, 111 (1937).

Some Flash-photolytic and Photochemical Studies of Retinene and Related Compounds[1a]

By Karl-Heinz Grellmann, Rudiger Memming[1b] and Robert Livingston

Flash illumination of air-free solutions of retinene produces a transient spectral response. The labile species, presumably the lowest triplet state of retinene, has a strong absorption band with a peak at 450 mμ. It disappears by a first order process. The value of the rate constant depends on the solvent, being, at room temperature, 9.6×10^4 for hexane and 4.3×10^4 sec.$^{-1}$ for glycerol. The rate decreases with temperature. The energies of activation are 0.9, 0.7 and 2.4 kcal. for hexane, toluene and glycerol, respectively. No spectral transients were observed when anaerobic solutions of a Schiff's base, a protonated Schiff's base or a hemiacetal of retinene were illuminated. Both the all-trans and the all-cis forms of the protonated Schiff's base of retinene and propylamine undergo rapid cis–trans isomerization when they are exposed in methanolic solution to white light.

Introduction

Abrahamson, et al., report[2] that flash illumination of all-trans retinene, in anaerobic tetrahydrofuran

(1) (a) This research was supported by the Division of Biology and Medicine of U. S. A. E. C. under Contract AT (11-1) 718. (b) Phillips Zentrallaboratorium GMBH, Hamburg-Stellingen.

or methyl cyclohexane, produces a short-lived transient species, which disappears by a first order process. Neither vitamin A nor a protonated

(2) E. Abrahamson, R. Adams and V. Wulff, J. Phys. Chem., 63, 441 (1959); E. Abrahamson, J. Marquisee, P. Gavuzzi and J. Roubie, Z. Elektrochem., 64, 177 (1960).

Schiff base of retinene and p-toluidine exhibits any such spectral response. The transient species of retinene has been tentatively identified as its lowest triplet state. We have confirmed these results and extended the measurements to other solvents and to temperatures in the range from 26 to −73°.

Materials.—The solvents (hexane, toluene and methanol) were high grade commercial preparations and were distilled before use. The glycerol was of U.S.P. grade and was twice vacuum distilled; a small amount of 1 N NaOH was added before the second distillation. The 11-cis and all-$trans$ retinene were purified samples, kindly furnished by P. Brown of the Harvard Biological Laboratories, to whom the authors are indebted.

The Schiff's base was prepared by dissolving about 1 mg. of retinene in 1 ml. of n-propylamine. After 10 minutes, 3 drops of the solution were transferred to a small flask, and the excess amine removed with a stream of dry nitrogen. The residue was dissolved in methanol, containing 0.1 M HCl.

Preparation of Solutions.—The solutions which were used in the flash-photolytic studies were degassed on a vacuum line. After boiling off about 5% of the solvent at room temperature or below, the solution was frozen with liquid nitrogen and the space above it was evacuated to the "black-vacuum" stage. The vessel then was closed off from the pump and allowed to warm up to room temperature. It was frozen again and once more evacuated. This process was repeated three or four times. Finally the solution was transferred to the cuvette by tilting part of the vacuum line, and the cuvette was sealed-off under vacuum.

Retinene, in alcohol or glycerol, is rapidly converted to a hemiacetal, if the solvent contains a trace of acid. This reaction is accompanied by a shift of the absorption maximum from about 380 to 320 mμ. The reaction is prevented if the glycerol is treated with NaOH, as described above, and if the cuvette is rinsed with dilute NaOH solution before use.

Apparatus.—The flash-photolytic apparatus which was used in the kinetic studies has been described.[3] The scanning light was rendered approximately monochromatic by means of a second-order interference filter. A filter with a peak transmission at 500 mμ was used for the solution in glycerol, and one with its peak at 470 mμ, for all other retinene solutions. The low-temperature measurements were made in a double-walled cylindrical cuvette. The coolant was circulated between the cylinders, and double windows were placed at the ends to prevent fogging. The absorption spectrum of the transient was determined with the aid of a flash-photolytic, flash-photographic apparatus modelled on that described by Breitschwerdt and Weller.[4]

Results

The transient form of retinene (in toluene) has an intense, apparently symmetrical absorption maximum near 450 mμ, certainly lying within the limits 445 to 455 mμ. An isosbestic point between the normal and transient spectra occurs near 404 mμ. Our measurements did not make possible a determination of the depopulation of the ground singlet state; however, a comparison of the absorption observed during the flash with the normal absorption spectrum indicates that at least 28% of the retinene was in its "triplet" state. If it is assumed that the conversion is 30%, the maximum extinction coefficient of the triplet is about 2.5 times the extinction coefficient of the ground state at its first maximum, λ380 mμ.

The absorption spectrum of all-$trans$ retinene was measured with a Cary spectrophotometer in several solvents, at ambient temperatures and at

(3) G. Jackson, R. Livingston and A. Pugh, *Trans. Faraday Soc.*, **56**, 1635 (1960).

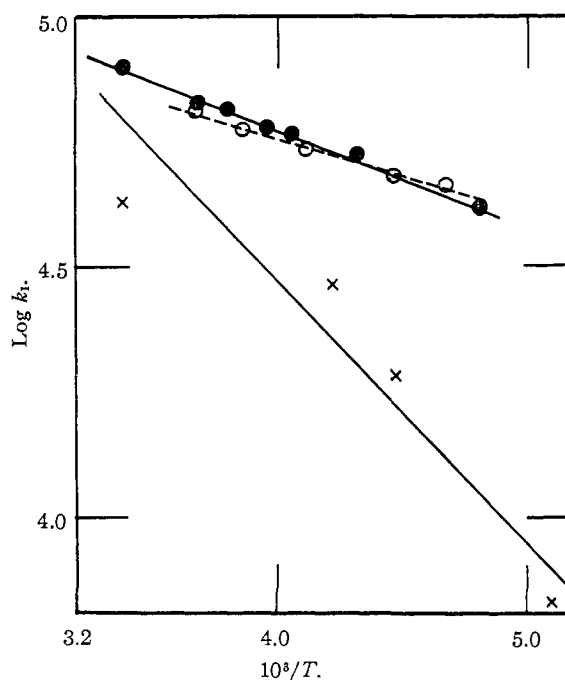(4) K. Breitschwerdt and A. Weller, *Z. physik. Chem. (N.F.)*, **20**, 353 (1959).

Fig. 1.—The rate of disappearance of the retinene triplet as a function of temperature, between 25 and −75°: ●●●, toluene; OOO, decalin; ×××, glycerol.

wave lengths between 300 and 500 mμ. Except for shifts in the position of the maximum, the spectra were similar. The peak was observed at these wave lengths: hexane, 360; decalin, 375; toluene, 380; methanol, 380; methanol + water (1:1 by volume), 390; water containing 1% digitonin, 390; glycerol, 400 mμ.

Within the limits of precision, the decay of the retinene triplet was first order in all solutions studied. The results of kinetic studies, using approximately 5×10^{-5} M solutions of all-$trans$ retinene, are summarized by Table I and Fig. 1.

TABLE I

DECAY OF THE RETINENE TRIPLET

Solvent	Temp., °C.	$k_1 \times 10^{-4}$ (sec.$^{-1}$)
Hexane	25	9.6
Tetrahydrofuran	25	7.2(1)
Toluene	26	7.9
Toluene	−73	4.2
Decaline	0	6.5
Decaline	−58	4.6
Methanol	25	6.0
Glycerol	23	4.3
Glycerol	−75	0.70

No transient spectral changes were observed when the solvent was either water containing 1% digitonin or a 1:1 mixture of methanol and water. Temperature had no effect upon the initial yield of the triplet when glycerol was the solvent, but the yield, measured in toluene or decalin, was about three-fold greater at low than at ambient temperatures. At room temperature the per cent. conversion to the triplet is about one-fourth as large in glycerol as in the hydrocarbon solvents. Measurements made with 11-cis retinene, in toluene and in decalin at room temperature, indicated that the
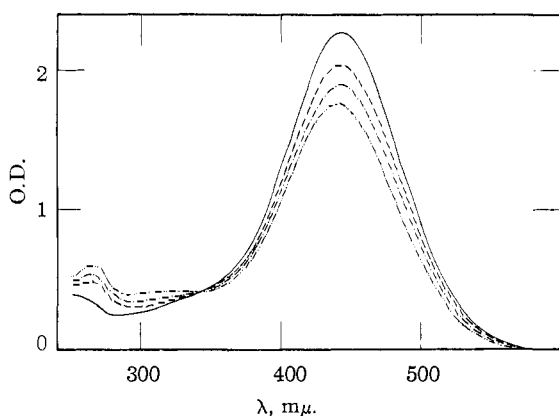
Fig. 2.—Photochemical stereoisomerization of the protonated Schiff base of all-*trans* retinene and *n*-propylamine in methanol: the optical densities were measured with a Carey Spectrophotometer: ————, before illumination; – – –, 10 sec. illumination; — – — –, 20 sec. illumination; — – – — – –, 90 sec. illumination.

mean life of the triplet does not differ significantly (± 15%) from those observed when all-*trans* retinene was used.

No transient spectral change was observed when deaerated solutions of the hemiacetal of retinene, the Schiff's base of retinene and *n*-propylamine, or the protonated form of this base were subjected to the same flash as was used in the retinene measurements. The solvents used in these experiments were hexane for the Schiff's base, and methanol for both the hemiacetal and the protonated base.

The data plotted on Fig. 1 demonstrate that the rate of decay (at least for toluene and decalin) conforms to the Arrhenius relation. The energies of activation are 0.9 ± 0.1, 0.7 ± 0.1, and 2.4 ± 0.8 kcal. for toluene, decalin and glycerol, respectively. The corresponding preexponential factors are 3.5 × 10^5, 3.0 × 10^5 and 2.5 × 10^6 sec.$^{-1}$. It is of interest[5] that the energies of activation are noticeably less than those which correspond to diffusionally limited bimolecular rates.

As is illustrated by Fig. 2, the protonated Schiff's base undergoes rapid *trans–cis* isomerization when it is illuminated. In these experiments approximately 2 × 10^{-5} *M* solutions in ordinary (undried) A.R. grade methanol, contained in 2 cm. quartz cells, were placed 15 cm. from a 60 watt tungsten lamp. The shift in the position of the main absorption peak is slight, but the reaction can be followed by the decrease in the optical density at this peak and the appearance of a *cis* peak at 267 mμ. It is not known what *cis* isomer or isomers are formed by this reaction. A similar but reversed spectral change occurs when a solution of the 11-*cis* form of the protonated base is illuminated. The quantum

(5) Compare G. Jackson and R. Livingston, *J. Chem. Phys.* (in press).

yield for the *trans–cis* reaction appears to be about two fold greater than the yield for the reverse process. Allowed to stand in the dark, the originally *cis* solution slowly continues to approach the all-absorption spectrum; but the all-*trans* solution tends to revert to its original form.

An 11-*cis* solution was exposed to full sun light for 30 minutes. Instead of approaching a stable, stereoisomeric steady state, both the main and the *cis* peak decreased to about two thirds of their original value and a new absorption band appeared at 320 mμ. This suggests that a relatively inefficient photochemical formation of hemiacetal occurred, under the conditions of the experiment.

Discussion

The fact that no spectral transients are observed, when solutions of vitamin A, retinene hemiacetal or protonated Schiff's bases of retinene are studied by the usual flash-photolytic method, is evidence that either the triplet state is not populated or that its mean life is less than 10^{-6} sec. Abrahamson, *et al.*, prefer the first of these alternative interpretations and blame the inefficiency of triplet formation upon the lack of a suitably situated n-π state. This interpretation leaves unexplained how the molecule loses its energy of excitation. Since vitamin A is only weakly fluorescent[6] and solutions of protonated Schiff's bases are not detectably fluorescent, the loss of excitation cannot be attributed to a radiative process. If the degradation of energy is the result of strong coupling between electronic oscillations and nuclear vibrations, fluorescence or phosphorescence should be readily detectable if these substances were dissolved in or adsorbed on rigid media.[7]

Protonated Schiff's bases of retinene and simple amines are commonly regarded as simplified model compounds for rhodopsin. It is of interest, therefore, that a solution of such a base is efficiently photoisomerized. It is also noteworthy that the positions of the absorption maxima, of the 11-*cis* and all-*trans* protonated Schiff's bases of retinene and *n*-propylamine, do not differ by more than 50 Å.

Compared to anthracene and dibenzanthracene,[4] the effect of temperature upon the mean life of the retinene triplet, in glycerol, is surprisingly small. The energies of activation for the decay of the triplet of retinene and of anthracene and for the change of viscosity of glycerol are about 2.5, 12 and 18 kcal., respectively. Also unlike anthracene, there is (in the range of temperatures covered) no evidence for the existence of a temperature-independent[4] component of the decay of the retinene triplet.

(6) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949, p. 428.

(7) T. Förster, "Fluoreszenz Organischer Verbindungen," Vandenhoeck and Ruprecht, Göttingen, 1950, pp. 116–122.