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Pyridinium Complexes. I. The Significance of the Second Charge-Transfer Band of Pyridinium Iodides

BY EDWARD M. KOSOWER, JOSEPH A. SKORCZ,¹ WILLIAM M. SCHWARZ, JR., AND JAMES W. PATTON

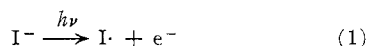
RECEIVED AUGUST 10, 1959

A second charge-transfer absorption band appears in the spectra of many pyridinium iodide complexes in non-polar solvents. Its relationship to the first charge-transfer absorption band² is shown by parallel behavior with respect to solvent variation and within limits, to change in the substituents on the pyridinium ring. The difference, ΔTE , between the transition energies for the two bands varies between 15.9 and 28.6 kcal./mole. However, ΔTE for 1-methylpyridinium iodide in chloroform is 21.8 kcal./mole. Franck and Scheibe⁴ interpret the ultraviolet spectrum of iodide ion as a photo-ionization process, producing an iodine atom and a "solvated electron." Two bands are observed with ΔTE 21.2 kcal./mole, corresponding closely to the expected difference for electronic transitions leading to an iodine atom, which has two low-lying energy states, $^2P_{1/2}$ and $^2P_{3/2}$, separated by 21.74 kcal./mole (0.943 ev.) as determined by analysis of iodine spectra. The close correspondence of the ΔTE value for 1-methylpyridinium iodide in chloroform to the ΔTE value expected for production of an iodine atom is direct evidence for the charge (electron)-transfer nature of the excitation in the pyridinium iodide. In addition, the position for the charge-transfer band of 1-methylpyridinium iodide in water can be derived from a plot of transition energies against Z , a standard of solvent polarity.³ The position thus derived (2561 Å.) demonstrates that the charge-transfer process is greatly facilitated by the 1-methylpyridinium ion, for iodide ion in water has a maximum

at 2259 Å. A complete description for the transition is thus: $MPy^+I^- \xrightarrow{h\nu} MPy \cdot I \cdot$. Systematic variations in ΔTE values are found for different types of iodide charge-transfer spectra, for which no rationalization is readily apparent.

In a previous paper, the existence of a second pyridinium iodide charge-transfer absorption band was mentioned.^{2,3} The purpose of the present paper is to show how the existence of the second band is in accord with the current model³ for pyridinium iodide charge-transfer transitions.

Halide ions are of particular spectroscopic interest because of their monatomic nature. Iodide ion in water has two absorption bands in the accessible ultraviolet region, at 2259 and 1937 Å. Franck and Scheibe proposed many years ago that the separation between the two band maxima corresponded to the separation between the two low-lying states of the iodine atom, the $^2P_{3/2}$ and $^2P_{1/2}$ states.⁴ The inference was clear that light absorption by iodide ion was equivalent to a photo-ionization. The Franck-Platzman theory of a potential well formed by solvent molecules serves as an adequate description of the location of the electron after excitation,⁵ although some controversy still exists on some of the details.⁶ Equation 1 illustrates the process for iodide.

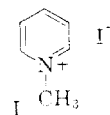


The difference between the two lowest states of the iodine atom was estimated originally by Franck from data on neon⁷ and was quickly confirmed by Turner.⁸ The most recent value is 0.943 ev. or 21.74 kcal./mole.⁹ The proposal of Franck and Scheibe may be generalized as follows: *Light ab-*

sorption by iodide ion which exhibits two bands separated by a characteristic energy difference, defined as ΔTE , leads to an excited state containing an iodine atom. An important qualification of the rule is that some binding, presumably small, exists between the iodine atom and the system to which the electron has been transferred. It should be noted that Katzin¹⁰ recently made an attempt to utilize the above rule for light absorption for any iodine compound, including polyiodide metal ion complexes and covalently bound iodo compounds. An experimental study of a few of the latter, to be reported elsewhere,¹¹ does not bear out such a generous extension of the rule. We shall regard the rule as applying only to iodide ion; even with this limitation, it seems likely that a narrow definition of the magnitude of ΔTE is not possible.

Results

In the course of an investigation of the charge-transfer bands of alkyl-substituted pyridinium iodides,¹² it was found that the second band for 1-methylpyridinium iodide (I) readily could be observed under carefully controlled experimental conditions. In pure chloroform, for example, the



long wave length maximum (first charge-transfer band) was at 3796 Å. (ϵ 1210) and the second maximum (second charge-transfer band) was located at 2945 Å. (ϵ 1550). The transition energy difference, ΔTE , between these two maxima was 21.8 kcal./mole, identical to that predicted for the formation of an iodine atom in the excited state⁹ within the experimental error. The spectrum of 1-methylpyridinium iodide is shown in Fig. 1.

(1) Based in part on a portion of a thesis submitted by Joseph A. Skorcz in partial fulfillment of the requirements for the M.S. degree, June, 1959.

(2) E. M. Kosower, *THIS JOURNAL*, **80**, 3253 (1958).

(3) This research was supported in part by funds granted by the Air Force Office of Scientific Research through Contract 49(638)-282, Grant No. E-1608 of the National Institute of Allergy and Infectious Diseases and the Wisconsin Alumni Research Foundation through the Research Committee of the Graduate School.

(4) J. Franck and G. Scheibe, *Z. Physik. Chem.*, **A139**, 22 (1928).

(5) R. Platzman and J. Franck, "L. Farkas Memorial Volume," Jerusalem, 1952, p. 21; *Z. Physik.*, **138**, 411 (1954).

(6) M. Smith and M. C. R. Symons, *Trans. Faraday Soc.*, **54**, 338, 346 (1958).

(7) J. Franck, *ibid.*, **21**, 536 (1925).

(8) L. A. Turner, *Phys. Rev.*, **27**, 397 (1926).

(9) K. Mirakawa, *Z. Physik*, **109**, 162 (1938).

(10) L. I. Katzin, *J. Chem. Phys.*, **23**, 2055 (1955).

(11) E. M. Kosower, Pih-kuci C. Huang, and W. M. Schwarz, Jr., unpublished results.

(12) E. M. Kosower and J. A. Skorcz, *THIS JOURNAL*, **82**, 2195 (1960).

A change in the solvent composition, effected by adding ethanol in increasing amounts to the chloroform, leads to a shift of the first maximum. In chloroform containing 0.97% ethanol, the first maximum for 1-methylpyridinium iodide is 3730 Å., while the second maximum is now found at 2890 Å. The difference, ΔTE , is 22.2 kcal./mole, somewhat higher than that for pure chloroform; however, examination of the data in Table I for 1-methylpyridinium iodide spectra taken in chloro-

TABLE I

VARIATION OF MAXIMA WITH ETHANOL CONTENT FOR 1-METHYLPYRIDINIUM IODIDE IN CHLOROFORM

Vol. % EtOH	λ_{\max}	ϵ_{\max}	E_T^a	ΔTE
0.0	3796	1210	75.3	21.8
	2945	1550	97.1	
.27	3796	1250	75.3	21.5
	2952	1570	96.8	
.54	3785	1220	75.5	21.7
	2942	1480	97.2	
.62	3778	1200	75.7	21.6
	2938	1480	97.3	
.72	3756	1190	76.1	21.9
	2918	1480	98.0	
.88	3738	1200	76.5	22.4 ^b
	2892 ^b	1560	98.9	
.97	3730	1190	76.7	22.2 ^b
	2890 ^b	1500	98.9	

^a Transition energy $2.859 \times 10^{-3} \nu$ (in cm^{-1}). ^b The proximity of this maximum to the sharply rising absorption band for the 1-methylpyridinium ion probably moves it to somewhat shorter wave lengths, thereby increasing ΔTE .

form solutions containing various amounts of ethanol suggests that ΔTE is substantially constant over the limited range available for consideration. Not only does ΔTE remain constant (or almost so) but the intensity relationship of the two bands is unaltered over the range of ethanol concentrations used. The remarkable solvent sensitivity of pyridinium iodide charge-transfer bands² requires that only a closely related band could maintain a constant energy separation.

The second band for all other alkylpyridinium iodides is only partially visible, due to occultation by the absorption of the pyridinium ring. For those cases in which a marked change in slope clearly indicated two types of absorption in the 2800–3100 Å. region, it was possible to obtain some idea

TABLE II

POLYALKYLPYRIDINIUM IODIDES

Substituent	λ_{\max}	ϵ_{\max}	E_T	λ^a	E^b	" ΔTE " ^c
1-CH ₃ ^d	3738	1200	76.5	3060	93.4	17
1,4-(CH ₃) ₂ -	3587	1240	79.7	2990	95.6	16
1,2-(CH ₃) ₂ -	3637	870	78.6	3010	95.0	16
1- <i>i</i> -CH(CH ₃) ₂ -	3705	1020	77.1	3010	95.0	18
1-CH ₃ -4- <i>n</i> -C ₃ H ₇ -	3598	1150	79.5	3020	94.7	15
1-CH ₃ -4- <i>i</i> -C ₃ H ₇ -	3593	1210	79.6	3015	94.8	15
1-CH ₃ -4- <i>t</i> -C ₄ H ₉ -	3590	1180	79.6	2980	95.8	16
1-C ₂ H ₅ -	3726	1150	76.7	3060	93.4	17
1-CH ₃ -4-C ₂ H ₅ -	3587	1190	79.7	2980	95.8	16

^a Wave length at which optical density was equal to that at λ_{\max} . ^b Transition energy corresponding to the wave length found according to ^a. ^c Estimated as ± 1 kcal./mole. ^d Solvent: chloroform containing 0.90% ethanol by volume.¹²

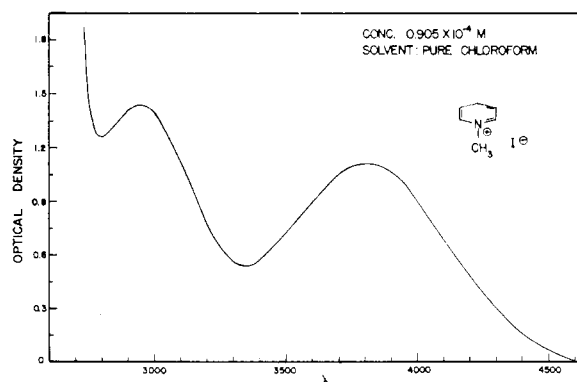


Fig. 1.—The spectrum of 1-methylpyridinium iodide in pure chloroform.

of the behavior of the second band by finding the wave length at which the absorption intensity became equal to that of the first charge-transfer band maximum. The differences thus found are listed as " ΔTE " in Table II and are certainly less accurate (± 1 kcal./mole) because the data for the second band were obtained from curves run at ordinary speed (5 Å./sec.)¹² The " ΔTE " values are 16 ± 1 kcal./mole with only one exception and represent agreement with the proposition that the second band is a charge-transfer absorption like the first.

For a change in substitution at a particular position on the pyridinium ring, *e.g.*, from 4-carbomethoxy to 4-cyano, the second band moves in the same direction as the first and roughly to the same extent (Table III).

TABLE III
 ΔTE VALUES AND IODIDE SPECTRA

Iodide	Solvent	λ_{\max}	ϵ_{\max}	E_T^a	ΔTE
Potassium	HOH	2259	12300	126.6	21.0
		1937	14300	147.6	
Sodium ¹²	HOH	2262	13500	126.4	21.4
		1935	13500	147.8	
Sodium	(CH ₃) ₂ CO	2551	12000 ^b	112.1	20.2
		2161	14700	132.3	
Pyridinium-1-CH ₃	Pure CHCl ₃	3796	1210	75.3	21.8
		2945	1550	97.1	
1-CH ₃ -2-CN	CH ₂ Cl ₂	4775	1200	59.9	21.1
		3528	2100	81.0	
1-CH ₃ -2-COOC ₂ H ₅ -	CHCl ₃ ^c	4270	1070	67.0	21.2
		3243	1475	88.2	
1-CH ₃ -3-COOCH ₃	CHCl ₃ ^c	4070	1850	70.2	15.9
		3320	1380	86.1	
	CH ₃ CN	3595	298	79.5 ^d	
		3361	1100	85.1	
1-CH ₃ -4-CN	CH ₂ Cl ₂	4905	1000	58.3	26.8
		3361	1100	85.1	
1-CH ₃ CH ₂ -4-COOCH ₃	ClCH ₂ CH ₂ Cl	4508	880	63.4	28.6
		3108	992	92.0	
Triiodide, (C ₂ H ₅) ₄ N	CH ₃ CN	3605	26100	79.3	18.8
		2915	50800	98.1	

^a Transition energy in kcal./mole. ^b Erroneously reported as 9330 in a previous article.¹⁴ ^c Containing 0.90% ethanol by volume. ^d Corresponds to a slope of 1.14 in E_T versus Z^2 , as compared to 1.12 for 1-methylpyridinium iodide¹² and 0.97 for 1-ethyl-4-cyanopyridinium iodide.²

The spectrum of potassium iodide in water was measured and showed a reasonably good agreement with the results of Lederle for sodium iodide.¹³ A small decrease in ΔTE was found along with the

(13) E. Lederle, *Z. physik. Chem.*, **B10**, 121 (1930).

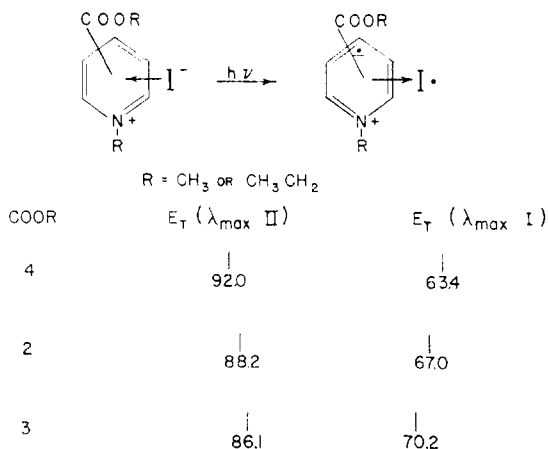


Fig. 2.—A diagram showing the relationships among the band pairs for pyridinium iodides substituted at different positions with the same group. The number immediately below the black lines is the transition energy in kcal./mole. (For data, see Table III.)

large shift in the maxima for sodium iodide in acetone. The change in the position of iodide absorption was previously reported only for the first band.¹⁴ These maxima are summarized in Table III.

Electron-withdrawing substituents on the pyridinium ring move the first charge-transfer band lengths.¹⁶ The relationship of the second band to the first band, that is, ΔTE , depends upon the position of the substituent. For 2-substituents, ΔTE is only slightly smaller than the value for 1-methylpyridinium iodide itself; for a 3-substituent, ΔTE is considerably lower than ΔTE for the parent iodide, while ΔTE for 4-substituents is much larger than expected. The unexpected variation in ΔTE requires further investigation; at present, the appearance, intensities and positions of the band pairs listed in Table III can be taken as favoring their interpretation as pairs of iodide charge-transfer bands.

Triiodide ion can be regarded as a readily dissociable complex of iodide ion and iodine molecule,¹⁶ and a thermodynamic analysis of its properties suggests that its absorption spectrum is intramolecular.¹⁷ Tetraethylammonium tri-iodide in acetonitrile has a ΔTE value of 18.8 kcal./mole, appreciably less than iodide ion in water or iodide ion complexed with 1-methylpyridinium ion (Table III).

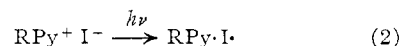
Discussion

The theoretical value of ΔTE is 21.74 kcal./mole.⁹ The values found for iodide ion in water (21.0 or 21.4 kcal./mole), iodide ion in acetone (20.2 kcal./mole),¹⁸ and iodide ion in proximity to a

1-methylpyridinium ion (21.8 kcal./mole) are reasonably close to the theoretical value, providing strong support for removal of an electron from the iodide ion in each case. The position of the first charge-transfer band of 1-methylpyridinium iodide in water may be estimated with confidence from a plot of transition energies against Z , a standard of solvent polarity.² The maximum in water is estimated as 2561 Å.,¹² showing that proximity of the 1-methylpyridinium ion greatly facilitates electron excitation away from the iodide ion. The effect of substituents on the pyridinium ring¹⁵ is direct evidence that electron-transfer is to the pyridinium ring. A similar comparison may be made for acetone solvent, where sodium iodide has a first maximum at 2551 Å. and the maximum in the presence of the 1-methylpyridinium ion may be estimated¹² at 3608 Å. (cf.¹⁸).

A model involving electron-transfer from the iodide ion to the pyridinium ring previously had been advanced to explain the unusually large solvent sensitivity of the first absorption band of pyridinium iodides.⁴ The present work is in accord with this model in that electron-transfer away from the iodide ion is shown by the Franck-Scheibe criterion (ΔTE) and electron-transfer to the pyridinium ring is indicated as described above. Direct evidence that the ground state is essentially an ion pair also has been obtained.¹⁹

The light absorption process for alkylpyridinium iodides then may be written with some confidence as



Another facet of the relationship between the two charge-transfer bands is illustrated in Fig. 2, in which it may be seen that the variation in the position of substitution for a particular group results in a change in the location of the second band of roughly the same magnitude as that of the first band but *opposite in direction*.

The ΔTE values listed in Table III are far from a random distribution around the number expected on the basis of the Franck-Scheibe rule. However, many more measurements will be necessary for a thorough classification of the ΔTE values. At present, no rationalization of the variations is readily apparent. It is of interest to note that alkali halides in the gas phase have ΔTE values slightly larger than the theoretical for pure electron-transfer away from iodide ion, with 22.6 kcal./mole as a typical value for sodium iodide.²⁰

Acknowledgments.—The authors wish to express their gratitude to Professor C. D. Cornwell, Chem-

work, the determination actually necessitates the use of very thin cells (0.010 cm.) with correspondingly higher concentrations of sodium iodide (ca. 0.01 M). It is uncertain, therefore, that electron transfer to an acetone molecule *alone* is important, and not, for example, to an acetone molecule coordinated with a sodium ion. Smith and Symons⁴ insist that *all* iodide excitations are of the water type¹ (unless specific complex formation can be measured) primarily on the basis of temperature effects. It is important to realize that the location of the electron in the excited state is the unsettled question, and not the nature of the transition, so that the position of the absorption bands is information of value, and ΔTE retains its physical significance.

(19) E. M. Kosower and W. M. Schwarz, Jr., unpublished results.

(20) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, "Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1950; cf. also L. E. Orgel, *Quart. Revs.*, **8**, 422 (1954).

(14) E. M. Kosower, *THIS JOURNAL*, **80**, 3261 (1958).

(15) The transition energies for the first band give a rather good straight line when plotted against the Hammett σ -constants, with ρ of +13.4. E. M. Kosower and J. A. Skorcz, paper presented at the Fourth Meeting of the European Molecular Spectroscopy Group, Bologna, Italy, September 9-14, 1959.

(16) L. I. Katzin and E. Gebert, *THIS JOURNAL*, **76**, 2049 (1954).

(17) In contrast to iodide, cf. eq. 1, H. L. Friedman, *J. Chem. Phys.*, **21**, 319 (1953).

(18) Although acetone possesses a sufficiently high dielectric constant (D 21.2) to support complete dissociation of sodium iodide ion-pairs at the concentration level usually used for ultraviolet absorption

istry Department, and to Dr. Emil Kazes, Physics Department, for valuable discussion concerning the origin of the variation in the ΔTE values. We wish particularly to thank Professor R. S. Mulliken, University of Chicago, for helpful criticism.

Experimental

Materials.—The preparation, purification and properties of 1-methyl- and other alkylpyridinium iodides are described in detail elsewhere.¹²

1-Methyl-2-cyanopyridinium Iodide.—A solution of 24.61 g. (0.236 mole) of 2-cyanopyridine (Aldrich Chemical Co., Milwaukee) and 30 cc. (0.48 mole) of methyl iodide in 40 cc. of nitrogen-flushed dry methanol was allowed to stand at room temperature for twenty-one days. The salt crystallized out as orange prisms. Purification was accomplished by dissolving the rather pure first product in water (1 cc./g.), adding acetone (10 cc./g.), and cooling to 0°. Orange platelets were filtered off; yield 31.0 g. (61.8%), m.p. 175–176° (vac., dec.) (reported as yellow crystals, m.p. 183–184°).²¹ Equiv. wt., calcd., 246.1; found, 245.6.

1-Methyl-2-carbomethoxypyridinium Iodide.—Ethyl picolinate (Fluka A.G., Buchs, St. Gallen, Switzerland) was treated with methyl iodide in absolute ethanol, producing

(21) R. I. Ellin, *THIS JOURNAL*, **80**, 6588 (1958). Repetition of the procedure used by Ellin (which is, in fact, the usual quaternization procedure) consistently gave 4% yield, not 36% as reported. In addition, some hydrogen cyanide is evolved during reflux and represents a potential hazard to the considerable number of people (perhaps 1 in 10) who are not able to detect this substance by its "characteristic odor."

bright yellow needles from isopropyl alcohol, m.p. 108.3–109.3° (to red liq.). *Anal.* Calcd.: C, 36.88; H, 4.12. Found: C, 36.86; H, 4.28.

1-Methyl-3-carbomethoxypyridinium Iodide.—Methyl nicotinate (gift of Nepera Chemical Co., Inc., Yonkers, N.Y.) reacted with methyl iodide in methanol, giving light yellow crystals from methanol-ether, m.p. 132.5–133.5° (reported 129.5–130.2°),²² equiv. wt., calcd., 279.2; found, 279.1.

Both 4-substituted pyridinium iodides listed in Table III have been described before.²

Tetraethylammonium triiodide, m.p. 139–141°, was recrystallized from ethanol (reported m.p. 142°²³).

Acetone was dried by distillation from 4A Molecular Sieve (Linde Products) and water was distilled from potassium permanganate solution.

Spectra.—Potassium iodide in water and sodium iodide in acetone were measured with a Cary Recording Spectrophotometer, Model 14, using 0.0102 cm. cells (matched). The maxima were reproducible and offered no particular difficulties in their determination.¹⁴

All other spectra were obtained with a Cary, Model 11. Spectro grade methylene chloride (freshly opened!) and acetonitrile (Matheson, Coleman and Bell) served as solvents. Ethylene dichloride was carefully purified¹⁹ and the chloroform had an alcohol content of ca. 0.90% unless otherwise indicated. Extraordinary care was exercised in the measurement of the data collected in Tables I and II and will be reported in detail in the accompanying publication.¹²

(22) L. Bradlow and C. A. VanderWerf, *J. Org. Chem.*, **16**, 1143 (1951).

(23) S. K. Ray and D. Majumdar, *J. Indian Chem. Soc.*, **14**, 197 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

Pyridinium Complexes. II. The Nature of the Intermediate in the Dithionite Reduction of Diphosphopyridine Nucleotide DPN

BY EDWARD M. KOSOWER AND SONIA W. BAUER

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The yellow intermediate formed in the dithionite reduction of DPN to DPNH is postulated to be a charge-transfer complex $DPN^+ \leftarrow SO_2^-$, on the basis of comparison of the spectra of intermediates derived from both 3- and 4-carbamidopyridinium ions and sodium dithionite.

One of the most important non-enzymatic reactions of the coenzyme DPN is the sodium dithionite reduction¹ to *enzymatically active* DPNH discovered by Warburg and his co-workers.^{2,3} Other reducing agents, e.g., electrolysis,⁴ X-rays⁵ and sodium borohydride,⁶ attack the pyridinium ring to form substances of low or zero coenzymatic activity. It is now firmly established that enzymatically active DPNH⁷ is a 1,4-dihydropyridine derivative.^{8,9}

(1) Supported in part by Grant E-1608 from the National Institute of Allergy and Infectious Diseases, National Institutes of Health.

(2) O. Warburg, W. Christian and A. Griesse, *Biochem. Z.*, **282**, 157 (1935).

(3) E. M. Kosower, S. W. Bauer and D. Goldman, Abstracts IV International Congress for Biochemistry, Vienna, September 1–6, 1958, No. 1-35.

(4) B. Ke, *Arch. Biochem. Biophys.*, **60**, 505 (1956); R. F. Powning and C. C. Kratzing, *ibid.*, **66**, 249 (1957).

(5) A. J. Swallow, *Biochem. J.*, **54**, 253 (1953).

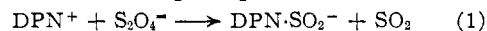
(6) M. B. Matthews, *J. Biol. Chem.*, **176**, 229 (1948); M. B. Matthews and E. E. Conn, *THIS JOURNAL*, **75**, 5428 (1953).

(7) DPN, diphosphopyridine nucleotide, DPNH, dihydrodiphosphopyridine nucleotide.

(8) M. Pullman, A. San Pietro and S. P. Colowick, *J. Biol. Chem.*, **206**, 129 (1954).

(9) R. F. Hutton and F. H. Westheimer, *Tetrahedron*, **3**, 73 (1959).

Von Euler and his group found that DPN and sodium dithionite gave yellow solutions under fairly basic conditions¹⁰ and Yarmolinsky and Colowick produced an elegant demonstration that the yellow color was due to an intermediate in the formation of DPNH, with the composition $DPN \cdot SO_2^-$, formed according to equation 1¹¹



Yarmolinsky and Colowick formulated the yellow intermediate as a 1,4-dihydropyridine derivative (I), but an analysis of its ultraviolet spectrum (Fig. 1) suggested that this might not be correct.¹² More recently, Wallenfels and Schüly¹³ have advanced a 1,2-dihydro structure on spectroscopic evidence for a crystalline "sulfinate" from dithionite and 1-(2,6-dichlorobenzyl)-3,5-dicarbamidopy-

(10) H. v. Euler, E. Adler and H. Hellström, *Z. physiol. Chem.*, **241**, 239 (1936); E. Adler, H. Hellström and H. v. Euler, *ibid.*, **242**, 225 (1936).

(11) M. B. Yarmolinsky and S. P. Colowick, *Biochim. et Biophys. Acta*, **20**, 177 (1956).

(12) E. M. Kosower, "The Enzymes," Vol. II, Academic Press, Inc., New York, N. Y., 1960, Chapter 13.

(13) K. Wallenfels and H. Schüly, *Ann.*, **621**, 178 (1959); *Angew. Chem.*, **70**, 471 (1958).