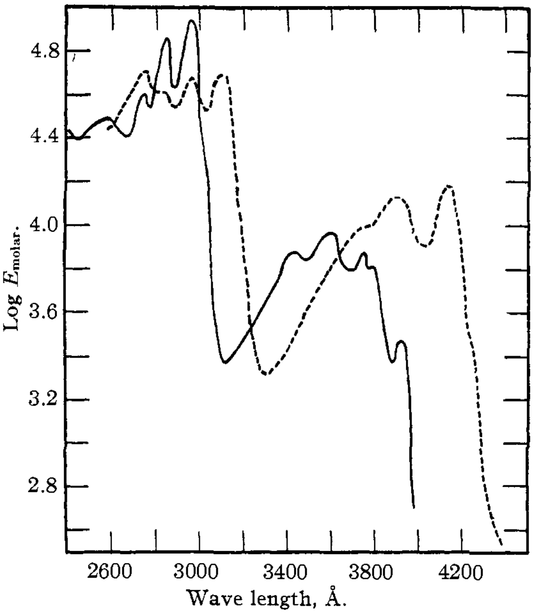

Fig. 2.—— ——,10-Thiocyanomethyl-1,2-benzanthracene; ----, 9-thiocyano-10-methyl-1,2-benzanthracene.

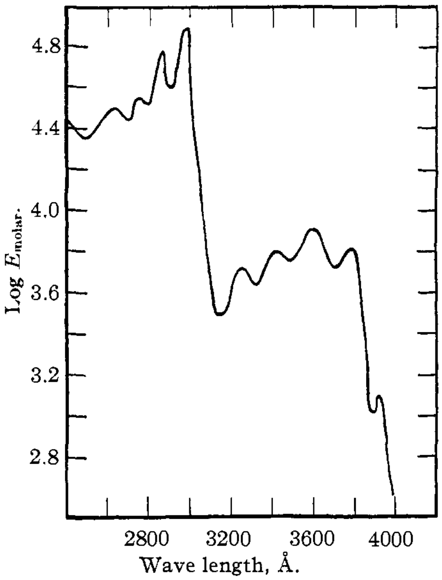

Fig. 3.—15-Thiocyano-20-methylcholanthrene.

1,2-benzanthracene and 1,2-benzanthracene indicates that in spite of the considerable chemical reactivity and unsaturation of the thiocyano group, its introduction does not significantly alter the excitation levels of the electrons of the aromatic ring system, and in this respect may be compared with the isocyanate group, the introduction of which likewise has little influence on the spectrum of 1,2-benzanthracene.[2] The spectra of ethyl thiocyanate and *n*-butyl thiocyanate[5] show only a low intensity maximum near 2500 Å. (log E = 1.6–1.7) and the additive effect of the thiocyano chromophore is negligible in comparison with that of the aromatic system.

The abnormal behavior of the 9-thiocyano derivatives may be attributed, most probably, to steric effects, the relatively large thiocyano group being under considerable restraint due to interference with the hydrogen atom at the 1′ position. This effect is not observed in 9-methyl-1,2-benzanthracene, probably on account of the smaller size of the methyl group, the spectrum of 4,5-dimethylchrysene, however, in which comparable steric conditions occur, differs from that of chrysene in a very similar manner.[6]

The spectrum of the thiocyano derivative of 20-methylcholanthrene closely resembles that of 1,2-benzanthracene and shows none of the abnormalities associated with a thiocyano substituent at the hindered meso position. The spectrographic evidence therefore favors the structure I in preference to II.

On irradiation with ultraviolet light in a dark room these compounds showed no fluorescence with the exception of the 10-thiocyano derivative which fluoresced bright green in the solid state and blue in solution. A sample of 9-methyl-10-thiocyano-1,2-benzanthracene showed similar fluorescence.

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Chlorophyll-Pheophytin: Temperature Coefficient of the Rate of Pheophytin Formation

BY G. MACKINNEY AND M. A. JOSLYN

As reported previously,[1] chlorophyll *a* reacts with acid 8–9 times as rapidly as chlorophyll *b*, in aqueous acetone solution. Measurements have now been made at various temperatures from 0–51° with suitable concentrations of oxalic acid. The pure chlorophyll components were prepared and measurements made as before.[1] At the higher temperatures, the solutions in stoppered test-tubes were rapidly cooled in an ice-bath immediately before measurement. In all cases, acid-free controls were measured under the same conditions. The reaction for each chlorophyll was run at three temperature levels with various concentrations of oxalic acid. Somewhat surprisingly, the plot of ln k/N (k is the first

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(5) Pestemer and Litschauer, *Monatsh.*, **65**, 239 (1935).

(6) Jones, THIS JOURNAL, **63**, 313 (1941).

(1) Mackinney and Joslyn, THIS JOURNAL, **62**, 231 (1940).

order rate constant, N the normality of acid) against $1/T$, the reciprocal of the absolute temperature, gave two virtually parallel curves, Fig. 1. We therefore prepared more chlorophyll a, the more abundant and more easily purified component, and repeated measurements at three intermediate temperatures. In view of the number of measurements at different time intervals, for the various acid concentrations, we are confident that the averages for k/N, Table I, are substantially correct.

TABLE I

EFFECT OF TEMPERATURE ON RATE CONSTANT

T, °K.	N	k	k/N	Av.
		Chlorophyll a		
273	0.01	0.410	41	
	.002	.098	49	45
280	.01	.522	46	
	.005	.222	52	49
295	.002	.221	110.5	
	.001	.108	108	109
301.5	.01	1.39	139	
	.007	0.907	129	
	.004	.539	135	
	.002	.211	105.5	127
310	.002	.676	338	
	.001	.373	373	356
324	.001	1.725	1725	1725
		Chlorophyll b		
273	0.05	0.23	4.6	
	.02	.04	2.00	3.3
301.5	.10	1.69	16.9	
	.05	0.804	16.1	
	.02	.328	16.4	
	.01	.148	14.8	16.1
324	.01	1.47	147	147

Explanations for the deviations of ln k at the higher temperatures (Fig. 1) from the expected straight line relationship include the possibility that secondary reactions occur without being detected. As pointed out by Zscheile and Comar,[2] a considerable proportion of the chlorophyll could be allomerized without affecting the phase test. Variation in the effect of solvent with chlorophyll may also be involved. Regardless, however, of the true explanation, there is no significant difference in the energies of activation for the two chlorophylls whatever basis we select for our calculations.

If we ignore the values for the higher temperatures, and take the slopes of the lines of best fit, we find from the expression

$$d \ln k = -(E/R)d\,(1/T)$$

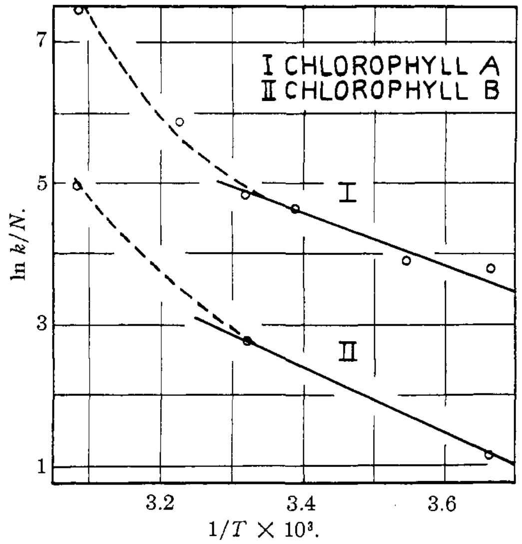

Fig. 1.—First order rate constants as a function of temperature: I, chlorophyll a; II, chlorophyll b.

energies of 7500 and 9000 cal. for chlorophylls a and b, respectively. If the values at 0 and 51° be selected, in the two cases, we obtain values of 12,500 and 13,000 cal., respectively. The similarity of these results indicates that the higher rate constant for chlorophyll a cannot be explained on the basis of a greater reactivity, and the most plausible explanation is the possibility of steric hindrance in the case of chlorophyll b. Phytol also, for example,[3] is less readily split off the chlorophyll b.

It is of interest that the stability of the magnesium is markedly affected by the state of oxidation of the isocyclic ring. Preliminary experiments indicate that the effect of a few drops of hydrogen peroxide is to cause a rapid increase in the reaction rate. We hope to report later on the effect of various oxidizing and reducing agents on the stability of magnesium, as this may provide clues to the remarkable ease with which chlorophyll disappears in many biological systems, under conditions as yet ill-defined.

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[2] Zscheile and Comar, *Bot. Gaz.*, **102**, 463 (1941).

[3] Weast and Mackinney, *J. Biol. Chem.*, **133**, 551 (1940).

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The Preparation of Hydrosols by Freezing

BY THOMAS J. SHEA, WILLIAM E. DOOLEY AND CLAUDE SCHWOB

In a previous investigation in this Laboratory[1] hydrosols of active charcoal were prepared by a

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[1] Schwob, THIS JOURNAL, **58**, 1115 (1936).