

TABLE III
PARACHOR VALUES OF BRANCHED CHAIN HYDROCARBONS

Alkane	P, n-isomer	P, exp.	Strain per branch
2-Methylheptane	351.0	349.4	-1.6
3-Methylheptane	351.0	347.7	-3.3
4-Methylheptane	351.0	347.6	-3.4
3-Ethylhexane	351.0	345.0	-6.0
3-Methylpentane	271.0	267.9	-3.1
Calculated from previously recorded data			
3-Ethylpentane	311.0	304.2	-6.8
2-Methylhexane	311.0	309.1	-1.9
3-Methylhexane	311.0	307.3	-3.7
2,5-Dimethylhexane	351.0	347.2	-1.9
2,4-Dimethylhexane	351.0	344.9	-3.1
2,3-Dimethylhexane	351.0	344.1	-3.5
3,4-Dimethylhexane	351.0	342.6	-4.2
2,4-Dimethylpentane	311.0	307.5	-1.8
2,3-Dimethylpentane	311.0	304.3	-3.4
2,5-Dimethylheptane	391.0	384.9	-3.1
2,4-Dimethylheptane	391.0	381.1	-5.0
2,3-Dimethylheptane	391.0	373.1	-9.0
2,7-Dimethyloctane	431.0	426.4	-2.3
2,4-Dimethyloctane	431.0	422.9	-4.1

the most compact structure would have the lowest parachor. The same effect may be noted in parachor values calculated from previously recorded densities and surface tensions of hydrocarbons.¹⁰ These values are also included in Table III. While certain regularities appear, sufficient data are not available to properly evaluate the variations in the effect of branching the chain.

Summary

1. The densities, surface tensions, and para-

(10) M. P. Doss, "Physical Constants of Principal Hydrocarbons," Third Edition, Texas Corp., 1942.

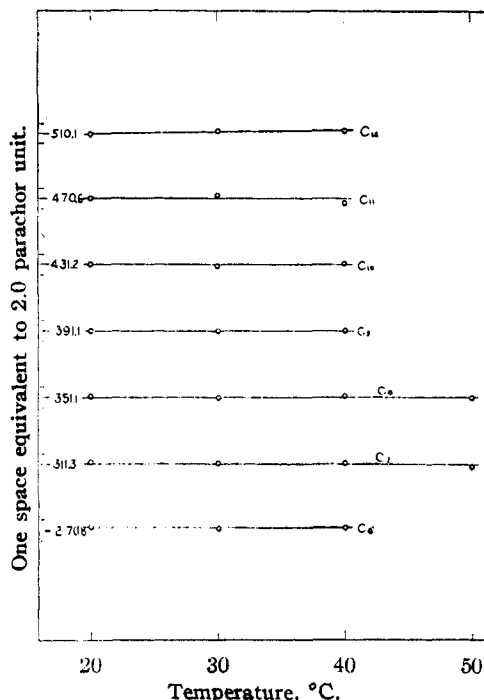


Fig. 3.—Parachors of normal hydrocarbons.

chors of a series of hydrocarbons of high purity have been reported.

2. The parachor value of the CH₂ group is reported as 40.0. The atomic parachor of H is reported as 15.5, that of C as 9.0.

3. There is no apparent change in the CH₂ increment as the chain is increased up to duodecane.

4. The effect of branching the chain is not constant in the saturated hydrocarbons

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A Spectrographic and Kinetic Study of the Alkaline Fading of Tetraiodophenolsulfonphthalein

BY EDWARD S. AMIS AND RALPH THEODORE OVERMAN

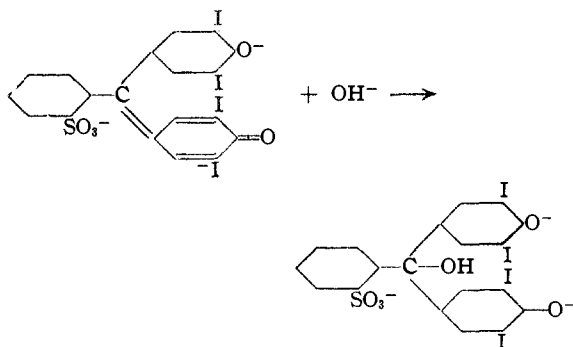
The alkaline form of iodo phenol blue (tetraiodophenolsulfonphthalein) has a characteristic absorption curve the intensity of which is a function of the amount of the dye present in the blue form. If an excess of the alkaline hydroxide is added to a solution of the iodo phenol blue, the dye fades to a colorless condition. The rate of fading depends upon the concentration of hydroxide present. When the colorless solution is acidified, the characteristic yellow acid form of iodo phenol blue develops progressively with time. This regeneration reaction has been studied quantitatively in the case of the brom

phenol blue.¹ It is possible to study the structure of the faded and unfaded form of the dyes both spectrographically and kinetically.

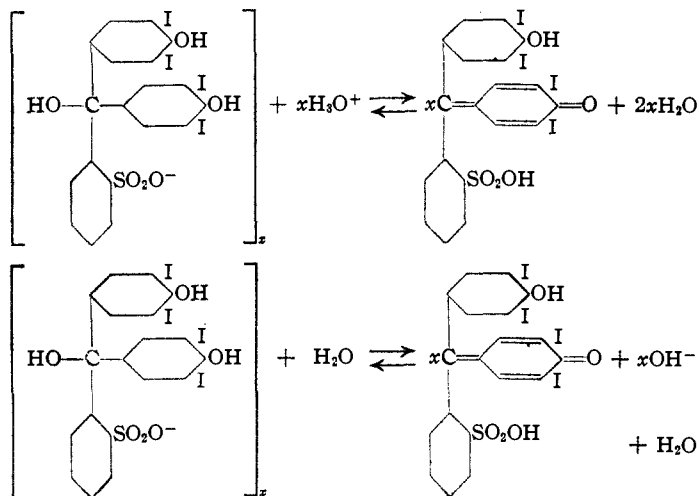
In this investigation a spectrographic study was made of both the unfaded and regenerated tetraiodophenolsulfonphthalein to determine whether the two were identical. A kinetic study of the fading process in the presence of iodide salt also was made. By these methods it was hoped that definite conclusions could be reached as to the validity of proposed mechanisms for the fading and regeneration processes.

(1) Amis and Price *J. Phys. Chem.*, **47**, 338 (1943).

I. **The Spectrographic Study.**—The fading is assumed to take place according to the reaction^{2,3}



and hence the regeneration is simply the re-forming of the colored quinoid form of the dye from the colorless carbinol. According to Brode⁴ the quinoid structure has a characteristic absorption band at a more or less definite region of the spectrum depending on the other groups present. The product formed in reaction (1) would show absorption due to the carbinol, phenol and sulfonic acid groups which have no absorption in the range of the normal photographic plate.⁴ The regeneration reaction it is presumed (1) takes place according to the following mechanisms



Thus the quinoid structure of the dye is regenerated and since this material is identical with the unfaded acid form of the dye, the absorption spectrum of the regenerated material should of necessity coincide with that of the acid form of the unfaded iodo phenol blue when the two are at like pH.

Apparatus and Procedure.—The spectrographic data were obtained using a large Littrow spectrograph with spectrometric attachments. For these experiments dye solutions were made

(2) Thiel, *Monatsh.*, **53/54**, 1008 (1929).

(3) Amis and LaMer, *THIS JOURNAL*, **61**, 905 (1939).

(4) Brode, "Chemical Spectroscopy," J. Wiley and Sons, Inc., New York, N. Y., 1939, pp. 127-142.

up to 10^{-5} molar using the same quality of dye and the same procedure employed by Amis and LaMer³ in studying the kinetics of the fading of bromo phenol blue. The alkali for the fading was made up according to the specifications of the above authors. All measurements were made from cells with a column of absorbing medium which was 2 cm. in length. The light source for the visible region was a Mazda filament lamp and for the ultraviolet region was a hydrogen discharge tube. The setting for the visible spectra was position 3 of the glass system covering a frequency of 450-700 fresnel units. For the ultraviolet absorption of the faded dye, positions 5 and 9 of the quartz system covering a region of 450-1500 fresnel units (2000-6000 Å.) were used.

The procedure consisted of printing a millimeter scale on the plate, exposing the plate as a blank with no absorption cells in the light beam, and then interposing the cells, one being filled with distilled water and the other containing the sample being studied and measuring the absorption. The respective cells for the water and for the sample were always the same. The blank was made necessary by the fact that it was found to be impossible to equate the light intensities of the two parts of the beam visually so that they gave identical readings on the densitometer. The

blank made it possible to correct for the initial difference in intensity of the two beams. The times of exposure were three, four and five seconds. The final curve was plotted from the average of the three densitometer readings corresponding to a given frequency.

The absorption as a function of the degree of fading was determined by setting the dye ($10^{-5} m$) to fade at room temperature in a known strength of alkali and at stated intervals of time measuring the absorption of the fading material. The fading was carried out in such concentrations of alkali that the short time used in taking absorption represented little change in the condition of the dye since the rate of fading was very slow.

The densitometer used was an Applied Research Laboratories Instrument which measures the density of the plate by use of a photoelectric cell. In this instrument the dark current is set to zero on the galvanometer scale and the reading of 100 as the transmission of a clear portion of the plate. The densitometer readings (D 's) then ranged from zero to one hundred.

The logarithm of the ratio of the galvanometer deflection (D) for the beam which had passed through the dye to that (D_0) which had passed through the water can be related to the absorption of the incident light by the dye solution when proper corrections are made for the corresponding deflections (D' and D'_0) obtained from the blank,

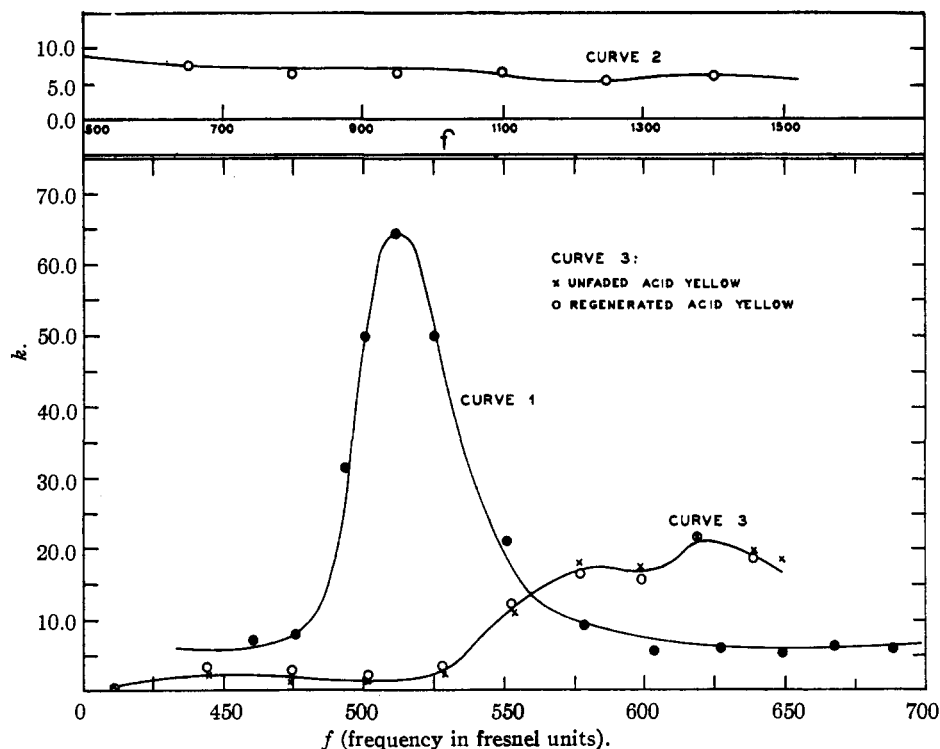


Fig. 1.—Specific extinction coefficient, k , versus frequency, f : Curve 1, monosodium salt of iodo phenol blue; Curve 2, iodo phenol blue faded in 0.009 molar sodium hydroxide; Curve 3, unfaded and regenerated iodo phenol blue in like strength of dilute hydrochloric acid.

and from this relationship we calculate the specific extinction coefficient, k , which according to Beer's law is given by

$$\log \frac{I}{I_0} = -kcd = \log \frac{D_0}{D} - \log \frac{D'_0}{D'}$$

or

$$k = \frac{1}{cd} \log \frac{DD'_0}{D_0D'}$$

This is plotted against frequency according to the suggestion of Brode.⁴

Data and Discussion.—The specific extinction coefficients and the corresponding wave lengths of the unfaded monosodium salt of iodo phenol blue (10^{-5} molar) in solution containing no excess alkali are plotted in Curve 1 of Fig. 1 using frequency in fresnel units as abscissas and specific extinction coefficients as ordinates. This method of plotting corresponds to decreasing wave lengths of light from left to right. The dye is seen to have a sharp absorption maximum at a frequency of 510 fresnel units or 5808 Å. The specific extinction coefficient as a function of frequency for the alkaline faded iodo phenol blue in 0.009 molar sodium hydroxide is plotted in Curve 2 of Fig. 1. This absorption spectrum is typical of non-chromophoric molecules, *i. e.*, molecules containing linkages similar to those found in alcohols, acids, etc.

The specific extinction coefficient as a function of frequency of both the unfaded and of acid

regenerated iodo phenol blue is likewise plotted in Curve 3 of Fig. 1, the measurements being taken in dilute hydrochloric acid solution of like concentration (pH 3) in both cases. The two spectra are identical and hence the regenerated dye corresponds exactly to the unfaded material. Thus the regeneration process is merely a change from the colorless carbinol to the yellow acid quinoid structure of the iodo phenol blue.

These spectrographic data would support the mechanism of the fading to be the formation of the colorless carbinol from the quinoid form of the dye as accepted by Thiel,² Biddle and Porter,⁵ Kober and Marshall,⁶ Kolthoff,⁷ and Amis and LaMer³ rather than the mechanism proposed by Kilpatrick and co-workers.^{8,9,10} These investigators thought that the fading was due to the substitution of one of the four iodine atoms in the dye molecule by the hydroxide ion yielding iodide ion.

Now if the fading mechanism were one of substitution of a heavier iodide atom by a lighter hydroxyl radical there should be only a shifting of the absorption band to correspond to the differ-

(5) Biddle and Porter, *THIS JOURNAL*, **37**, 1571 (1915).

(6) Kober and Marshall, *ibid.*, **33**, 59 (1911).

(7) Kolthoff, "Acid Base Indicators," The Macmillan Co., New York, N. Y., 1937, translated by Rosenblum from the fourth, 1931, German edition; see pages 111, 116 and 218-227.

(8) Chase and Kilpatrick, *THIS JOURNAL*, **54**, 2284 (1932).

(9) Kilpatrick, *Chem. Rev.*, **16**, 57 (1935).

(10) Panepinto and Kilpatrick, *THIS JOURNAL*, **59**, 1871 (1937).

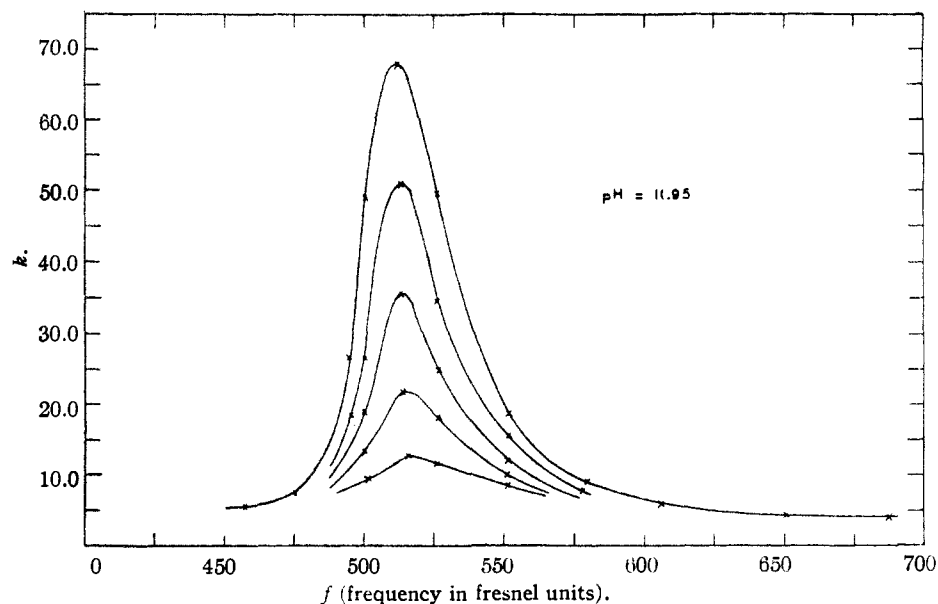


Fig. 2.—Specific extinction coefficient, k , versus frequency, f , of fading iodo phenol blue in 0.009 molar sodium hydroxide.

ence in resonance of the molecule. The absorption, however, would still be in the visible. Curve 2 of Fig. 1 shows that the faded form of the dye is non-chromophoric and has, therefore, lost its quinoid structure. Further, the regenerated acid form of the dye is identical in absorption with the acid form of the unfaded dye as shown by Curve 3 of Fig. 1. It appears that the acid regeneration is the removal of the hydroxyl radical from the carbinol and the reforming of the quinoid structure of the dye, rather than the re-entering by acidification of the iodine atom into the benzene nucleus.

Figure 2 represents the absorption of the iodo phenol blue as a function of the degree of fading in 0.009 molar sodium hydroxide. These curves strongly resemble the absorption of the phthalein dyes as a function of the pH of the solution.¹¹ And as in the case of change of pH , the absorption band does not shift greatly in wave length but simply changes in intensity, with the increased fading of the dye.

II. The Kinetic Study.—The fading of brom phenol blue as a function of hydroxide ion concentration has been carefully studied.³ In helping to prove the mechanism of the reaction it would be pertinent to study the salt effect upon the reaction velocity. Especially would it help if the rate were run in the presence of an iodide salt, since if the mechanism proposed by Kilpatrick, *et al.*, is correct the iodide ion should exert a mass effect whereas if the fading is due to the formation of carbinol the iodide salt should exert a primary salt effect and increase the reaction rate since the reactants are both negatively charged. Panepinto and Kilpatrick¹⁰ found a

(11) Brode, *THIS JOURNAL*, **46**, 581 (1924).

primary salt effect upon the rate constants for the fading of the chloro, bromo, and iodo phenol blue dyes in the presence of potassium chloride and bromide but found the values for the internal energy were not of sufficient accuracy to test the primary salt effect upon this function.

Materials and Procedure.—The materials and methods in these studies were essentially those used by Amis and LaMer.³ The stock solution of iodo phenol blue was 1×10^{-4} molar. The sodium iodide (J. T. Baker analyzed) was made up before each run by weighing on an analytical balance and diluted to a suitable volume. The temperature was held constant to $\pm 0.01^\circ$.

Ten milliliters of the 1×10^{-4} molar dye solution was placed in a volumetric flask and sufficient sodium iodide solution, sodium hydroxide solution and water were added to make a total volume of 100 milliliters of solution which was 1×10^{-5} molar with respect to the dye, 0.006 molar with respect to the sodium hydroxide and with such concentrations of sodium iodide as to give the various ionic strengths used in the studies. The time of addition of sodium hydroxide was noted and used as the initial time in the runs. A standard neutral solution of the dye (1×10^{-5} molar) was also made up and placed in the thermostat. To make a reading five milliliters of the fading dye solution was pipetted into one colorimeter cup and five milliliters of the standard unfading dye into the other colorimeter cup. Using a Klett top-reading colorimeter the amount of fading was determined as a function of time. The illumination used was a Mazda lamp with a blue filter.

The rate constants were calculated using the pseudo-unimolecular rate equation. The bimolecular rate constant was obtained by dividing the pseudounimolecular rate constant by the molarity of the sodium hydroxide which remained sensibly constant throughout a given run. The concentration was expressed in moles per liter and the time in days.

In Table I are tabulated the bimolecular rate constants at various ionic strengths and for the temperatures 25, 35 and 45° ; also the energies of activation and the Arrhenius frequency factors are recorded in this table. The quantitative agreement of the data on the rate constants with the requirements of Brönsted's theory of primary salt effect can be illustrated by plotting $\log k$ vs. $\sqrt{\mu}$ (see Fig. 3).

TABLE I

DATA FOR WATER WITH ALKALI HYDROXIDE AND ALKALI SALT ADDED: DYE $10^{-5} M$, NaOH 0.006 N WITH ADDED NaI

		k , 25°	k , 35°	k , 45°	ΔE^* , 25-35°	ΔE^* , 35-45°	B , 25-35°	B , 35-45°
0.000	0.0000	(14.3)	(27.7)	(50.2)	12,070	11,520	10.00	9.61
.006	.0775	19.7	38.5	69.9	12,180	11,640	10.24	9.84
.008	.0895	20.8	40.6	73.9	12,190	11,660	10.28	9.87
.010	.1000	21.6	42.2	76.9	12,210	11,680	10.32	9.91
.012	.1096	22.6	44.2	80.6	12,230	11,700	10.34	9.96
.016	.1265	24.0	47.0	86.0	12,250	11,730	10.37	10.01

$\log k$ obeys the limiting law to a higher ionic strength than would ordinarily be expected as was found for the alkaline fading of brom phenol blue by Amis and LaMer.³ Plots can be made of the energies and Arrhenius frequency factors, respectively, as a function of ionic strength. The slopes of these curves agree well with the limiting values of the slopes given by the equations¹²

$$\begin{aligned} \Delta E^* &= 1569 \sqrt{\mu} \text{ (temperature } 30^\circ) \\ \Delta E^* &= 1605 \sqrt{\mu} \text{ (temperature } 40^\circ) \\ \Delta S^*/2.3R &= 3.19 \sqrt{\mu} \text{ (temperature } 30^\circ) \\ \Delta S^*/2.3R &= 3.25 \sqrt{\mu} \text{ (temperature } 40^\circ) \end{aligned}$$

There is no indication that mass action is influential in the observed kinetics with added sodium iodide.

Conclusions

1. Absorption spectrum data on the alkaline faded iodo phenol blue show that the absorption approximates that of alcohol, acids or water. This would be expected if the carbinol were formed during the fading process.

2. Absorption spectra of the unfaded and regenerated acid solution of the dye are identical and it would appear that the fading process is reversed in acid solution.

3. The absorption of the fading dye as a function of the degree of fading, shows no marked shift in the absorption band during the fading process, but only a decrease in the intensity of absorption.

4. The influence of added sodium iodide upon the kinetics of the fading of iodo phenol blue is that of the Brønsted primary salt effect rather than a mass action effect.

5. These observations lead to the conclusion that the fading process is one of carbinol formation with the corresponding disappearance of the

(12) LaMer and Kammer, *THIS JOURNAL*, **57**, 2662 (1935).

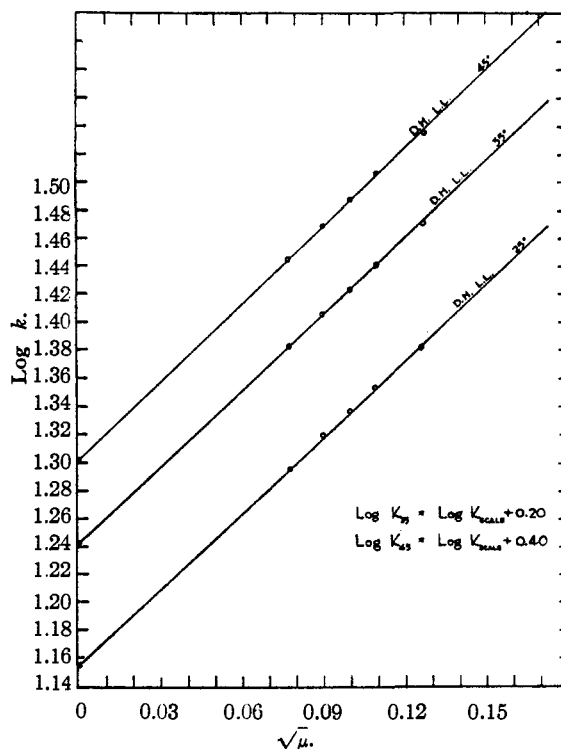


Fig. 3.— $\log k$ versus $\sqrt{\mu}$ for the alkaline fading of iodo phenol blue in 0.006 molar sodium hydroxide and various concentrations of sodium iodide.

quinoid structure and that the regeneration process is the reconstruction of the quinoid form of the dye.