Summary

1. Tin tetraphenyl reacts with (*a*) halogens to form aryl mono halides, (*b*) acyl halides to form phenyl ketones, (*c*) sulfur to form diphenyl sulfide, diphenyl disulfide and thianthrene. The reactions with alkyl halides and sulfuryl chloride were not conclusive. With nitric acid nitrobenzene was isolated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE DISSOCIATION INTO FREE RADICALS OF SUBSTITUTED DIXANTHYLS. V. THE RATE OF DISSOCIATION[1]

BY JAMES B. CONANT AND MILDRED W. EVANS[1]

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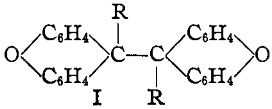
More than a dozen derivatives of dixanthyl of the type represented by Formula I have been prepared and studied in this Laboratory.[2]



I

(R = an alkyl or aryl group)

All of them in solution absorb oxygen at room temperature and in many cases the reaction is so rapid that the speed of the process is limited only by the rate of solution of the gas. However, those compounds in which the substituting group may be represented as RCH_2CH_2— are much less rapid in their action and it is possible, therefore, to study their auto-oxidation at room temperature. A few approximate measurements of the rate of oxidation of these substances were made in connection with their preparation; these results have been reported in the previous papers of this series. In order to learn more about the nature of the reaction, we have now undertaken a more detailed study of the auto-oxidation of a typical representative of the class, di-*n*-butyldixanthyl. The results of this investigation, which we are about to describe, led to the unexpected conclusion that we were in reality measuring a rate of dissociation into free radicals. Since the relation between this rate and the tendency of the compound to dissociate on heating is a matter of great interest, we continued the work and included a study of a number of homologs of di-*n*-butyldixanthyl at different temperatures. A discussion of the results so obtained forms the concluding portion of this paper.

In the case of many compounds which are appreciably dissociated in

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[1] This paper is part of a thesis presented by Mildred W. Evans at Radcliffe College for the degree of Doctor of Philosophy.

[2] Conant and co-workers, THIS JOURNAL, **47,** 572, 3068 (1925); **48,** 1743 (1926); **49,** 2080 (1927).

solution below 100°, the reaction with oxygen at 25° (in solution) proceeds almost quantitatively according to the reaction

$$R_3C{-}CR_3 + O_2 \longrightarrow R_3C{-}O{-}O{-}CR_3$$

The maximum amount of oxygen absorbed is one mole per mole of substance and a crystalline peroxide may be isolated in amounts as large as 80% of the theoretical. Such is the case, for example, with dibenzyldixanthyl, which absorbs oxygen very rapidly in solution. There seems to be no reason to believe that there is any fundamental difference between such a reaction and the slower oxygen absorptions of such compounds as di-*n*-butyldixanthyl. Indeed, it is possible to isolate the peroxide in this case, also, although the yield is poor. There is, however, another side reaction involving further oxidation of the peroxide or some intermediate oxide, since the total amount of oxygen absorbed corresponds to more than one mole. In the case of some of the alkyl dixanthyls as much as 2.5 moles of oxygen can be absorbed by prolonged exposure of the solution to oxygen. The susceptibility of the first oxidation product to further oxidation obviously accounts both for the low yields of peroxide and the increased oxygen consumption. We may, therefore, regard the measured rate of oxygen absorption of di-*n*-butyldixanthyl as the sum of the relatively fast normal reaction and a slower secondary oxidation which becomes appreciable only after the reaction has proceeded for some time. This is illustrated in Fig. 1, in which the rate of oxygen absorption of di-*n*-butyldixanthyl over a long period of time was measured (Curve A). For the first half mole of oxygen absorbed this curve corresponds to that of a monomolecular reaction (Curve B). Assuming this to be the major reaction, the Curve C represents the slower side reaction which is responsible for the diminution in yield of peroxide.

We have centered our attention on a study of the rate of the oxygen absorption in that range (0 to 0.6 of a mole of oxygen) in which the side reaction mentioned above appears to be negligible. We have calculated the fraction of dixanthyl derivative which has reacted at any given time from the volume of oxygen absorbed at that time and the calculated volume corresponding to 100% peroxide formation. This procedure introduces no error in the range in which the side reaction is negligible.

In Table I are collected representative measurements from our preliminary study of the factors affecting the speed of the reaction. The differential pressure apparatus employed was that described in detail later in this paper. At the time these measurements were made the experimental error was of the order of 10%, although later experiments reduced this to about 3%. The di-*n*-butyldixanthyl was dissolved in bromobenzene and the solution shaken with a large excess of air or oxygen. The volume of oxygen absorbed was calculated from the change in pressure. The concentration of dissolved oxygen throughout a given experiment was constant and therefore if the reaction were bimolecular, of the type $A + O_2 \longrightarrow AO_2$, the rate would nevertheless correspond to a first-order reaction. However, if the composition of the gaseous phase is changed, the concentration of dissolved oxygen must change. Thus, if the rate-controlling step involved the interaction of oxygen and the organic molecule, the rate should increase about five-fold on changing from air to oxygen. Actually there was no change (compare 1 and 2, 3 and 4, 5 and 6, in Table I). This fact shows that the combination with oxygen must be relatively fast and that

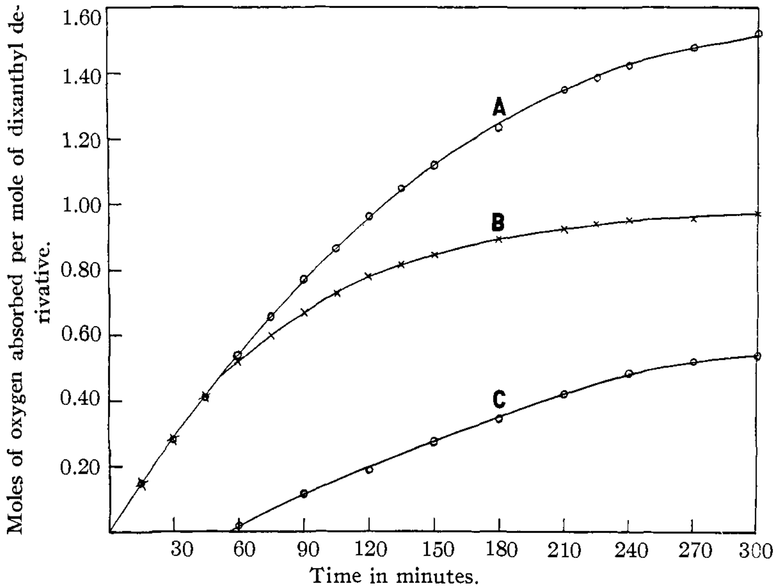


Fig. 1.—Rate of oxygen absorption of dibutyldixanthyl at 25° in bromobenzene solution. Curve A, observed rate; Curve B, calculated from first-order equation to correspond with A during first part of reaction; Curve C, difference between A and B.

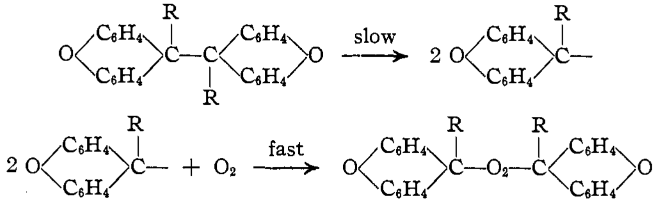
TABLE I

THE RATE OF OXYGEN ABSORPTION OF DI-*n*-BUTYLDIXANTHYL

Expt.	Temp., °C.	Gas	Concn. of dixanthyl deriv., *M*	Fraction of dixanthyl derivative reacted in 10 min.	15 min.	20 min.	30 min.	45 min.	Remarks
1	15	Air	0.01	...	0.10	...	0.13	0.15	0.29 at 2 hrs.
2	15	Oxygen	.01	...	.05	...	.12	.14	.28 at 2 hrs.
3	25	Air	.01	0.09	.13	0.17	.23		
4	25	Oxygen	.01	.11	.14	.17	.26		
5	25	Air	.01	...	.15	...	.26	.35	.45 at 60 min.
6	25	Oxygen	.01	...	.15	...	.28	.38	.49 at 60 min.
7	25	Oxygen	.005	.11	.15	.19	.30	.42	.53 at 60 min.
8	25	Oxygen	.003	.10	.15	.20	.30	.42	.55 at 60 min.
9	25	Oxygen	.002	.10	.14	.20	.29	.40	.54 at 60 min.

some slower reaction of the organic material alone controls the speed of the process. The reaction is of the first order with regard to the dixanthyl derivative (Expts. 6, 7, 8, 9, Table I).

Taking into account all that is known concerning the behavior of dixanthyl derivatives, it appears fairly certain that the rate-controlling step is the dissociation of the dixanthyl into free radicals. The mechanism of the oxygen absorption thus appears to be as follows



It is not surprising that the reaction is not subject to those marked catalytic effects which have been noted with so many auto-oxidation processes since it really is not an auto-oxidation which we are measuring. This lack of catalytic influence was clear both from the reproducibility of the results using different samples of dixanthyl compound and bromobenzene and also from the fact that no change was caused by the addition of 0.005% of hydroquinone, 3% of copper-bronze powder, powdered glass or a trace of sodium cyanide. It is further evident why the reaction has a rather unusually high temperature coefficient of the reaction velocity (an increase of 4–5-fold for 10° rise). The dissociation of a carbon–carbon linkage is the sort of process that might be expected to have a high temperature coefficient.

Having established to our own satisfaction the mechanism of the reaction, we then proceeded to a careful study of the rate of the dissociation of the simple alkyl derivatives of dixanthyl. The compounds studied were dimethyldixanthyl, diethyldixanthyl, dipropyldixanthyl, di-*n*-butyldixanthyl, di-*n*-amyldixanthyl and di-*iso*-amyldixanthyl. They were prepared and purified by the method described in earlier papers of this series. They were stored in an atmosphere of hydrogen in sealed ampules. Experiments with samples of the same compound prepared and purified at different times showed that the results were reproducible.

Apparatus and Procedure

The reaction vessel consists of a tincture bottle of 50-cc. capacity fitted with a ground-glass stopper carrying an entrance tube which was connected to one side of a manometer by means of about 10 cm. of heavy rubber tubing. Another bottle of the same shape and size was similarly connected with the other side of the manometer. Both bottles fitted into a holder which was immersed in a water thermostat and which was rocked back and forth by a suitable mechanism driven by a small motor. The manometer was of capillary glass tubing and contained bromobenzene colored with methylene blue. The difference in pressure was read on a millimeter scale placed directly beside the capillary tubing. The temperature of the thermostat was constant within ±0.1° and the bottles were completely immersed in the water.

In starting an experiment both bottles were charged with the same volume of bromobenzene (usually 4.0 cc.), oxygen bubbled through for five minutes from a tank, the stoppers quickly inserted and sealed with paraffin. The bottles were then placed in the holder and shaken until the manometer reading was constant; this required from ten minutes to half an hour. This equilibration of the solvent is essential if one wishes to obtain reproducible results with an accuracy of a few per cent. When equilibrium had been established, a sample (about 0.02 g.) of dixanthyl derivative was rapidly weighed to a tenth of a milligram in a small bulb with a long neck. This bulb was quickly introduced into the reaction bottle, which was removed from the thermostat and opened for a few seconds for this purpose. The stopper was sealed as before and the bottle placed in the thermostat for five minutes. During this time the sample did not come in contact with the solvent since the neck of the bulb-tube rested against the side of the vessel, keeping the tube upright. The levels of the manometer were now made equal by bringing both sides to atmospheric pressure by means of two three-way cocks. The cocks were then turned so that each side of the manometer was connected directly to one bottle. The bulb tube was now broken by one or two rapid shakes of the reaction bottle, which was immediately replaced in the holder and the shaking device started. The time was taken from this point and the manometer read. To assist in the rapid breaking of the bulb-tube a sharp pointed rod was usually inserted in the bulb-tube before it was placed in the reaction vessel. The solid dixanthyl derivative dissolves very rapidly; the error introduced by the time required for complete solution is probably slight and affects only the first few readings.

From the change in pressure as read on the manometer the volume of oxygen which has been absorbed may be calculated. In order to do this it is necessary to know the volume of gas displaced by the rise of the liquid in the manometer tube. This was found, by weighing a column of mercury, to be 0.006 cc. per centimeter. The total volume above the solution on each side of the system was 62 cc. The fraction of dixanthyl derivative which has reacted at any given time is equal to the volume of oxygen absorbed divided by the amount calculated on the assumptions in regard to the reaction discussed above (one mole of oxygen per mole of substance). The expression for this fraction, Z, in terms of the data just given and the difference in pressure expressed in millimeters of mercury, b, the barometric pressure P, the vapor pressure of C_6H_5Br, β, the weight of sample, w, and the molecular weight of the material (M.W.) is given in Equation 1, which is readily derived by an application of the gas laws.

$$Z = \frac{62b(0.0054P - 0.0054\,\beta + 62) - (0.0027)^2b^3}{(62 + 0.0027b)RT} \times \frac{\text{M. W.}}{w} \tag{1}$$

The term $(0.0027)^2b^3$ in the numerator and $0.0027b$ in the denominator may be neglected since b is never greater than 10. Variations in the barometric pressure between 750 and 770 mm. introduce errors less than the probable error of our measurements; the vapor pressure of bromobenzene may also be neglected. Taking an average value of P as 760, neglecting the terms just mentioned and substituting $m/9.05$ for b, where m is the pressure difference in millimeters of bromobenzene, we have Equation 2.

$$Z = 1.172 \times 10^{-4} m \frac{\text{M. W.}}{wT} \tag{2}$$

Discussion of Results

A few typical experiments are reported in full in Table II. The same results are shown graphically in Fig. 2, in which $-\log(1-Z)$ (where Z = fraction reacted) has been plotted against the time in minutes. The straight line was drawn to pass through the greatest number of points. The slope of this line multiplied by 2.303 is the value of k, the usual velocity constant of a first-order reaction. Using this value of k, values of Z have been calculated corresponding to the experimental points. The agreement between the values thus calculated and those found is shown in the last columns of Table II. It is evident that the reaction rate corresponds within the experimental error to that of a monomolecular reaction over the range studied. It will be noted that in Fig. 2 the straight lines do not pass through the origin. This is probably because the initial time is uncertain, in part due to the time required for solution of the material. By using this graphical method of obtaining the best value of k, this error has been largely eliminated. The two curves A and B in Fig. 2 and the corresponding data in Table II were chosen as representative of the most satisfactory and the least satisfactory of our duplicate experiments.

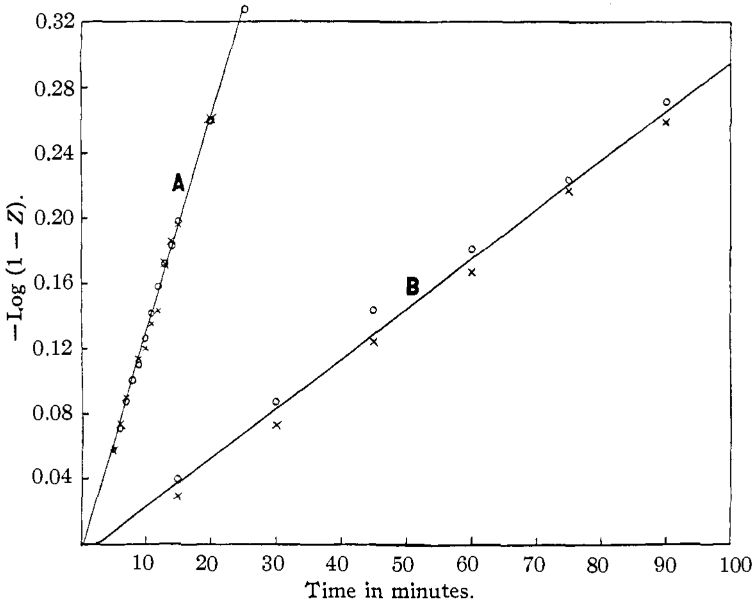


Fig. 2.—The rate of dissociation of dixanthyl derivatives as measured by rate of oxygen absorption: typical results. Curve A corresponds to Expt. 1, Table II; Curve B to Expt. 2; the crosses and circles indicate the points in the two duplicate runs.

TABLE II

TYPICAL DATA OBTAINED IN DUPLICATE EXPERIMENTS

(A) Substance = di-*n*-amyldixanthyl; solvent = bromobenzene; temp. = 35°.

Time, min.	Press., mm. of C_6H_5Br, *m*	Frac. reacted, *Z*	Frac. reacted, calcd., $k = 30.6 \times 10^{-3}$	Diff.	Time, min.	Press., mm. of C_6H_5Br, *m*	Frac. reacted, *Z*	Frac. reacted, calcd., $k = 30.6 \times 10^{-3}$	Diff.
		Expt. 1					Expt. 2		
5	14	0.124	0.128	−0.004	5	13.5	0.125	0.128	−0.003
6	17	.150	.157	− .007	6	17.0	.157	.157	0
7	20.5	.181	.182	− .001	7	20.5	.189	.182	+ .007
8	23.5	.208	.208	0	9	25.0	.231	.231	0
9	25.5	.225	.231	− .006	10	26.5	.242	.254	− .012
10	28.5	.252	.254	− .002	11	29.0	.268	.277	− .009
11	31.5	.278	.277	+ .001	12	30.5	.281	.298	− .017
12	34.5	.305	.298	+ .007	13	35.5	.327	.320	+ .007
13	37.0	.327	.320	+ .007	14	37.5	.346	.344	+ .004
14	39.0	.344	.344	0	15	39.5	.364	.360	+ .004
15	41.5	.366	.360	+ .006	20	49.0	.452	.444	+ .008
20	51.0	.451	.444	+ .007	25	57.0	.526	.526	0
25	57.5	.508	.526	− .018					

Expt. 1, $Z = 0.008839\ m$ (from Equation 2 by substituting values for *w*, M. W., *T*). Expt. 2, $Z = 0.009223\ m$.

(B) Substance = di-*n*-amyldixanthyl; solvent = bromobenzene; temp. = 25°.

Time, min.	Press., mm. of C_6H_5Br, *m*	Frac. reacted, *Z*	Frac. reacted, calcd., $k = 6.95 \times 10^{-3}$	Diff.	Time, min.	Press., mm. of C_6H_5Br, *m*	Frac. reacted, *Z*	Frac. reacted, calcd., $k = 6.95 \times 10^{-3}$	Diff.
		Expt. 1					Expt. 2		
15	9.5	0.087	0.081	+0.006	15	7.0	0.066	0.081	−0.015
30	20.0	.183	.174	+ .009	30	16.5	.155	.174	− .019
45	31.0	.283	.255	+ .028	45	26.5	.249	.255	− .006
60	37.5	.342	.330	+ .012	60	34.0	.320	.330	− .010
75	44.0	.402	.396	+ .006	75	41.9	.394	.396	− .002
90	50.7	.464	.456	+ .008	90	48.0	.450	.456	− .006
105	56.0	.511	.510	+ .001	105	54.0	.507	.510	− .003

Expt. 1, $Z = 0.009135\ m$; Expt. 2, $Z = 0.009396\ m$.

In Table III are summarized all of our final measurements. The values of *k* were obtained by the graphical method illustrated by Fig. 2. We consider the value of *k* for each compound at each temperature to be subject to an error of not more than ±3%.

In Fig. 3 the values of log *k* are plotted against the reciprocal of the absolute temperature, the slope of each line multiplied by 2.303 being the value of E/R in the equation $\mathrm{d}\ \ln k/\mathrm{d}T = -E/RT^2$. The values of *E* calculated from the integrated form of this equation are given in Table III. The average values for the dimethyldixanthyl (34,000) and diethyldixanthyl (29,000) are higher than the average for all the other compounds (26,000–27,100). This difference appears to be outside the experimental error. It is perhaps significant that the larger value of *E* corresponds to

TABLE III

SUMMARY OF RESULTS

All measured in bromobenzene; concn. = 0.01 *M*, oxygen employed.

Subs. and its m. p., °C.	Temp., °C.	No. of expts.	Total no. of points	Av. value of $k \times 10^3$ (graphically)	*E* in cal. 15–25°	25–35°	25°–40°	Average
Dimethyldixanthyl,	25	2	21	1.79		35,700		
179–180°	35	3	13	12.6			32,200	34,000
	40	2	15	24.3				
Diethyldixanthyl,	25	2	19	1.99		27,700		
191–193°	35	2	14	9.09				29,000
	40	2	17	23.1			30,400	
Di-*n*-propyldixan-	25	3	16	11.9		26,700		26,700
thyl, 179–180°	35	2	16	51.4				
Di-*n*-butyldixanthyl,	15	4	34	2.48	29,700			
162–163°	25	2	18	12.6		25,200		
	30	2	13	26.3			24,400	
	35	2	8	50.0				
	40	2	12	90.4				26,000[a]
Di-*iso*-amyldixan-	25	2	12	9.99				
thyl, 161°						26,200		26,200
	35	2	10	42.0				
Di-*n*-amyldixanthyl,	25	2	16	6.95				
94–96°						27,100		27,100
	35	2	25	30.6				

[a] Values for 15 to 30° (27,300) and for 30 to 40° (23,300) included in this average.

a lower value of *k* at a given temperature, though the ratio E/T_x (where T_x = the temperature at which $k \times 10^3 = 10$) varies from 110 for the methyl compound to 87.5 for the *n*-butyl compound. It seems unlikely that all this variation in E/T_x is due to experimental errors.

It is evident from Table III and Fig. 3 that the methyl and ethyl compounds cannot be distinguished the one from the other by our measurements. On passing from the ethyl to the *n*-propyl compounds there is an increase in *k* of six-fold, the normal propyl and butyl compounds are practically identical in their rates, but the *n*-amyl compound is somewhat slower. On the other hand, the *iso*-amyl compound is almost as rapidly dissociated as the *n*-propyl and *n*-butyl. The relationship between these higher homologs at 25° is $n\text{-}C_5H_{11}:iso\text{-}C_5H_{11}:C_3H_7:C_4H_9$ as 1:1.4:1.7:1.8. The practical identity in behavior of the methyl and ethyl compounds is somewhat surprising. In connection with the problem of the relationship between structure and speed of dissociation (the *k* of Table III), it must be remembered that di-*iso*butyldixanthyl (R = $(CH_3)_2CHCH_2$-) and dibenzyldixanthyl (R = $C_6H_5CH_2$-) absorb oxygen too rapidly for accurate measurements at room temperature (values of $k \times 10^3$ estimated as > 300) and the di-*iso*propyldixanthyl is appreciably dissociated in solution at room temperature and behaves like hexaphenylethane.

The parallelism between the rate of dissociation and the temperature required for appreciable dissociation (as judged by the color) in a 0.05 *M* solution is shown in Table IV. We have also included in this table some tests made by Dr. A. W. Sloan in this Laboratory on the rate of the reaction between a chloroform solution of the dixanthyl derivative and a dilute aqueous solution of ferric chloride and potassium ferricyanide. This reaction results in the more or less rapid formation of Prussian blue, presumably by virtue of the oxidation of the dixanthyl derivative to the corresponding carbinol and the reduction of the iron compound. If this reaction proceeds through the free radical (as it certainly does in certain cases),[3] the rate of the process might, like the rate of oxygen absorption, be controlled by the rate of dissociation. The results given in Table IV indicate that this is probably the case.

It is clear from an inspection of Table IV that the measurements of the rate of oxygen absorption, the Prussian blue test and the appearance of color on heating, all place the compounds in the same groups and that the differences in each case are of the same order of magnitude. If ΔH for the dissociation is approximately the same for all dixanthyl derivatives, the figures in Col. 4 of Table IV may be taken as an indication of the order of the relative values of log K at 25° since $d \ln K/d(1/T) = \Delta H/R$. The higher temperature corresponds to the larger value of $-\log K$. Since the dissociation constant $K = k_{\text{diss.}}/k_{\text{ass.}}$, it is interesting that from Table IV there appears to be at least a rough parallelism between $k_{\text{diss.}}$ (the rate of dissociation) and the equilibrium constant, K. This suggests the possibility that the speed of association of the free radicals (in solution) is practically the same for all these related compounds. This might well be the case if the rate of association of these very reactive molecules were limited only by the number of collisions; this number would be essentially independent of the chemical nature of the free radicals themselves.

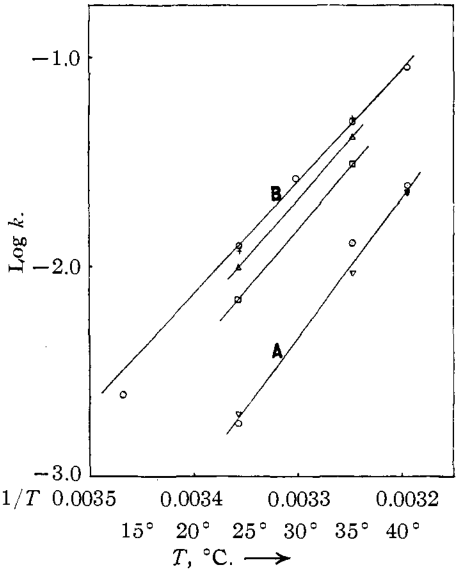


Fig. 3.—The rate of dissociation of dixanthyl derivatives at different temperatures. Line A, ○, dimethyldixanthyl; ▽, diethyldixanthyl. Line B and two shorter lines, ○, di-*n*-butyldixanthyl; +, di-*n*-propyldixanthyl; △, di-*iso*-amyldixanthyl-; □, di-*n*-amyldixanthyl.

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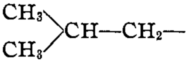
[3] Conant, This Journal, **47**, 1959 (1925).

TABLE IV

COMPARISON OF THE RATE OF DISSOCIATION OF DIXANTHYL DERIVATIVES AND THE TEMPERATURE REQUIRED FOR APPRECIABLE DISSOCIATION

Subs. groups	Approx. rate of diss. in C_6H_6Br at 25°, $k \times 10^3$	Time req. for Prussian Blue Test (see below), min.[a]	Temp.[b] at which "appreciable color" dev. in a 0.05 M soln. in $C_6H_5COOC_2H_5$
CH_3	2	35	210°
C_2H_5		..	
n-C_4H_9	10	20	160°
n-C_3H_7		..	
iso-C_5H_{11}		15	
$C_6H_5CH_2$—	Estimated >300	0.2	100°
 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH—CH_2—$		..	

[a] The Prussian blue test was carried out as follows: a few milligrams of the substance was dissolved in 3 cc. of chloroform and placed in a test-tube with 5 cc. of a very dilute aqueous solution of ferric chloride and potassium ferricyanide. The mixture was shaken vigorously for one minute and then allowed to stand. In the case of the most reactive dixanthyl derivatives there was an almost immediate formation of a blue precipitate; with the less reactive compounds the precipitate slowly formed at the interface between the solvents.

[b] The temperatures recorded in the fourth column were estimated by rapidly heating 0.05 M solutions (in $C_6H_5COOC_2H_5$) sealed in an inert atmosphere to 100, 160, 190, 210° and estimating the color by comparison with standards of dilute potassium dichromate solution. We estimate that the yellow color taken as "appreciable color" corresponds to about 1% dissociation but this value is, of course, very uncertain. Since all the experiments were performed exactly alike we feel that the relative temperatures required for the same degree of dissociation are significant and are probably correct within ±5°. The color due to dissociation was, of course, lost on cooling. Further information in regard to the reversible thermal coloring of the solutions has been given in the earlier papers of this series.

We hope to obtain further information along this line as a result of the studies which are now in progress in this Laboratory on the energetics and kinetics of free radical formation.

Summary

1. The rate of oxygen absorption of di-*n*-butyldixanthyl in bromobenzene solution at 25° has been measured by means of a differential pressure apparatus. The reaction is of the first order until about half a mole of oxygen per mole of dixanthyl derivative has been absorbed. The rate is independent of the concentration of the oxygen in the solution. It thus appears that the rate-controlling step is the dissociation of the dixanthyl derivative into a free radical.

2. The rates of dissociation of the following dixanthyl derivatives in bromobenzene have been measured at different temperatures by following the rate of oxygen absorption: dimethyl, diethyl, di-*n*-propyl, di-*n*-butyl,

di-*n*-amyl, di-*iso*-amyl. The energy of activation has been calculated from the temperature coefficient of the reaction velocity.

3. A parallelism has been found between the rates of dissociation and the temperature at which appreciable dissociation first occurs as evidenced by the appearance of color in a dilute solution.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

PHENANTHRENEQUINONES RELATED TO ALIZARIN AND PURPURIN

BY LOUIS FREDERICK FIESER

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It is an interesting indication of the general difference in the chemistry of anthracene and of phenanthrene that alizarin was synthesized, produced commercially and the structure established all in the course of seven years, while over fifty years have elapsed since the first attempt was made[1] to obtain the corresponding phenanthrene derivative and the substance has not yet been described. Phenanthrenequinone is so sensitive to the action of alkalies, acids and oxidizing agents that it is doubtful if many of its derivatives will prove useful as dyestuffs; but the angular alignment possesses a greater chromophoric character than anthraquinone, and it is at least a matter of theoretical interest to know how the phenanthrenequinones having two or more hydroxyl groups in the ortho and para positions compare with the anthraquinone dyes.

Morpholquinone, the first substance of this type to be described, was obtained by Vongerichten[2] from a degradation product of morphine. Because it was a mordant dye similar to alizarin, Vongerichten at first regarded it as 1,2-dihydroxyphenanthrenequinone, but later[3] recognized it as the 3,4-isomer. The aim of several investigators to prepare this quinone from phenanthrene, or by applying the Pschorr synthesis, was finally achieved by Schmidt and Söll.[4] An unsuccessful attempt to synthesize 1,2-dimethoxyphenanthrene, from which 1,2-dihydroxyphenanthrenequinone might be obtainable, has been recorded,[5] and Mukherjee and Watson[6] found it impossible to hydroxylate 2-hydroxyphenanthrenequinone by the methods so useful for the preparation of alizarin and its congeners. Thus no dihydroxyphenanthrenequinones possessing dyeing properties, other than morpholquinone, were known until Brass under-

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[1] Graebe, *Ann.*, **167**, 143 (1873).

[2] Vongerichten, *Ber.*, **32**, 1521 (1899).

[3] Vongerichten, *ibid.*, **33**, 352 (1900).

[4] Schmidt and Söll, *ibid.*, **41**, 3696 (1908).

[5] Pschorr and Buckow, *ibid.*, **33**, 1829 (1900).

[6] Mukherjee and Watson, *J. Chem. Soc.*, **109**, 617 (1916).