electrons must attain ionizing speed in a shorter distance than the mean free path.

3. Certain points were obtained at some multiple of the ionization potential plus 4.0 volts. This corresponds to a strong absorption band in chlorine and it is suggested that this may be one resonance potential of chlorine.

4. The relation of the ionization potentials of iodine, bromine and chlorine to one another is discussed.

5. It is suggested that the point at 8.2 volts in the case of chlorine corresponds to the formation of a molecular ion.

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STUDIES IN CHEMICAL REACTIVITY
II. THE ANTHRACENE $\leftrightarrows$ DIANTHRACENE REACTIONS, PHOTOCHEMICAL AND THERMAL

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On exposure to sunlight a solution of anthracene in benzene produces dianthracene, as was first shown by Fritzsche in 1866.

The photo-polymerization and thermal depolymerization processes have been examined in considerable detail by Luther and Weigert,[1] the investigation being continued by Weigert as well as by Byk,[2] the latter from the theoretical standpoint only. Earlier work is cited in the papers referred to. The considerations involved in these modes of treatment belong to a period at which the possibility of viewing the processes from the point of view of the quantum theory had not yet been recognized. It is of interest, therefore, to see to what conclusions a quantum treatment, as expressed in the radiation hypothesis of thermal change, leads.

Luther and Weigert used in general the mercury vapor lamp as a source of illumination, the anthracene solutions being enclosed in glass vessels so that presumably the ultraviolet region was cut off and the effects (such as the polymerization) are to be attributed, in agreement with Luther and Weigert themselves, to the violet end of the visible spectrum.

It is stated by Perrin[3] that while photo-polymerization is going on the solution fluoresces in the "indigo-violet." This would correspond approximately to a wave length of about $450\mu\mu$.

Incidentally, the velocity of thermal depolymerization of dianthracene at more than one temperature has been more completely investigated

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[1] Luther and Weigert, *Z. physik. Chem.*, **51**, 297 (1905); **53**, 385 (1905).

[2] Byk, *ibid.*, **62**, 454 (1908).

[3] Perrin, *Ann. phys. chim.*, **10**, 133 (1918); **11**, 1 (1919).

by Luther and Weigert in the case of phenetole than in any other solvent. For this reason we have restricted ourselves for the present to the behavior of the anthracene-dianthracene system in this solvent.

An examination in this Laboratory of the absorption of anthracene in phenetole in the *visible* region has shown the existence of *two* rather narrow bands at 475$\mu\mu$ and 445$\mu\mu$, approximately. For purposes of calculation we have to take the mean of these two values, namely 460$\mu\mu$. Incidentally, phenetole itself shows a band, fairly broad, with its head at 505$\mu\mu$. These values though not exact are sufficiently accurate for the immediate purpose in view. Since under the conditions employed no sensible amount of dianthracene is present, it is to be concluded that anthracene itself can absorb at the "mean" region 460$\mu\mu$. At the same time this is the region of fluorescence which is ascribed by Perrin to the existence of and in fact to the act of decomposition of the *di*anthracene molecule. The energy corresponding to 460$\mu\mu$ is 61,300 cals. per mole of the fluorescing substance, whichever it may be.

According to the radiation hypothesis of chemical change the energy *emitted* by a dianthracene molecule[4] in the act of depolymerization should be identical with the critical increment or energy of activation of *two* anthracene molecules. This follows from the relation between critical increments and heat of reaction.[5]

On the simplest basis we should expect that two anthracene molecules, being identical in nature, would have to be activated to the same extent to form a molecule of dianthracene. In other words we should expect that anthracene dissolved in phenetole would exhibit a band at 2 × 460 or 920$\mu\mu$. This region is not very amenable to investigation, but in so far as an instrument of the radio-micrometer type can be employed in this region the measurements recorded later have entirely failed to detect a band. The absorbing power of anthracene has been examined from 0.8μ to 3.8μ. Although the solution shows a band at 0.9μ this is indistinguishable from the absorption of the phenetole itself at this point. The complete curve (Fig. 1) will be considered later.

From the spectroscopic results we must conclude that the individual molecules of anthracene can absorb at the 445–475$\mu\mu$ region. If we assume that *the polymerization process as ordinarily carried out involves essentially the activation of a molecule of anthracene to the high degree represented by the mean wave length 460$\mu\mu$, namely 61,300 cals., and that this molecule then combines with a non-activated molecule to give the polymer,* we obtain a result which is in agreement with other quantitative considerations to be discussed later.

In passing, it may be mentioned that Perrin, in ascribing the phenom-

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[4] Not to be confused with the critical increment of the dianthracene molecule.

[5] Compare Lewis, *J. Chem. Soc.*, **111**, 457 (1917).

enon of fluorescence to the act of decomposition of the dianthracene molecule considers the fluorescence as essentially a property of the latter. In view of the absorbing power of the anthracene itself it would seem necessary to regard the fluorescence as belonging to an activated molecule of anthracene, the fluorescence being in fact a manifestation of the return of certain of these molecules to the normal state. Other workers[6] have likewise attributed the fluorescence to the anthracene molecule.

Absorption of Anthracene in the Short Infra-red Region

The measurements were made with a Hilger infra-red spectrometer using a radio-micrometer as the measuring instrument. The mode of procedure was the same as that described in a previous paper,[7] namely, a comparison of the transmission of light of a given wave length through each of two cells of different thicknesses containing the solvent or solution. To avoid local heating, the liquid under examination passed continuously through the cells. The ratio of the transmissions gives the fractional transmission and consequently the percentage transmission for the solvent or the solution at the given wave length. These transmissions are then plotted against wave length for both solvent and solution.

For both solvent and solution the examination was made over the range 0.8μ to 3.8μ. The resulting percentage transmission curves (Fig. 1) were repeated several times and showed a degree of reproducibility to within ±0.3% in the percentage transmission observed. Results exceeding this limit of reproduction were again examined over the whole range.

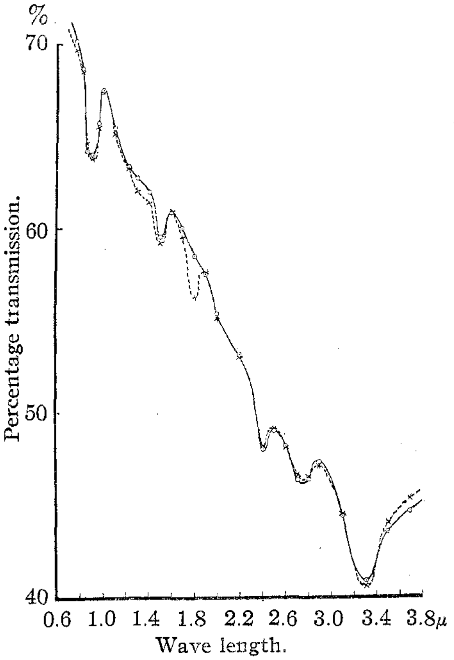

Fig. 1.—Phenetole (continuous). Anthracene solution (dotted), net thickness of layer = 0.214 cm.

The solution of anthracene employed was saturated at about 12°, and contained approximately 3 g. per 100 cc. of solution. The weakness of this solution did not necessitate any allowance being made for the effective

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[6] Compare Miss L. S. Stevenson, *J. Phys. Chem.*, **15**, 845 (1911).

[7] *J. Chem. Soc.*, **121**, 665 (1922).

thickness of solvent in the thickness of the solution examined, the same pair of cells in both cases being employed. The resulting transmission curves are superimposed as shown in the figure, so that any shift of the solution curve relative to the solvent curve could easily be detected.

The phenetole curve itself (continuous line) shows bands at 0.9μ, 1.5μ, 2.4μ, 2.75μ and 3.3μ. On comparing these with the data given by Coblentz[8] for its analog anisole which exhibits bands at 1.7μ, 2.4μ, 2.75μ and 3.32μ, we find good agreement, notably in the amount of shift of the benzene band, namely, from 3.25μ to 3.3μ, due to the alkyl group. The only distinctive difference between the solvent and solution transmission curves occurs at 1.8μ where the solution curve shows a band quite apart from that of the solvent. Over the remainder of the curve the agreement is excellent save in the region 1.3μ where the difference though apparently real—the difference appeared repeatedly—lies just on the limit of experimental error.

We conclude, therefore, that anthracene is capable of absorbing at 1.8μ, that is, at a frequency which is very nearly one-fourth of that to which the actual polymerization is attributed, namely, 460$\mu\mu$ mean. If the 1.8μ band were effective one would expect polymerization to occur as a *thermal* phenomenon, that is, slowly in the dark. Since this does not happen to a detectable extent, it seems reasonable to conclude that the 460$\mu\mu$ band is in fact the photochemically effective one.

In view of the somewhat unexpected behavior of anthracene, which necessitates the assumption that in the photo-polymerization process *one* molecule is activated and the *other* unactivated, and in view also of some rather vague references made by Luther and Weigert regarding the existence of intermediate complexes, it was considered advisable to ascertain whether the solute, anthracene, exists in phenetole solution in the simple molecular form or whether a thermal polymer exists which differs in some way from that produced photochemically. Careful molecular-weight determinations were therefore carried out by Mr. H. Millet in this Laboratory using the micro-differential tensimeter of Smits.[9] Millet found that anthracene undoubtedly exists in phenetole in the simple normal molecular form.

The Critical Increment of Dianthracene

We are here considering the critical increment or energy of activation of the dianthracene molecule in respect to depolymerization.

According to Weigert the concentration of the dianthracene in thermal equilibrium in solution *increases* as the temperature is raised. That is, dianthracene is formed with absorption of heat, the magnitude of this

[8] Coblentz, "Investigations of Infra-red Spectra," *Carnegie Inst. Pub.*, **1905**, Part I.

[9] Smits, *Z. physik. Chem.*, **39**, 385 (1902).

heat effect being approximately 20,000 cals. per mole.[10] Applying the radiation hypothesis to the thermal reaction, one molecule of dianthracene $\longrightarrow$ 2 molecules of anthracene, we have: Heat evolved = critical increment of resultant *minus* critical increment of reactant = E (for 2 mols. anthracene) $-E$ (for 1 mole of dianthracene). Inserting the numerical values we obtain: $20,000 = 61,300 - E$ (dianthracene), whence E per mole of dianthracene is approximately 41,300 cals.

That this result is correct may be shown by making use of the velocity-constant data of the depolymerization process actually measured by Luther and Weigert. With phenetole as solvent, the observed temperature coefficient over the range 160° to 170° is 2.8, whence E per mole of dianthracene is 39,200 cals. From an inspection of the velocity constant data it is concluded that the probable error is about 2000 cals. It is legitimate, therefore, to conclude that the calculation of the critical increment of dianthracene by two independent methods (independent in so far as experimental data are concerned) leads to very concordant values. The mean value of E for dianthracene is in round numbers 40,000 cals. per mole. The agreement obtained indicates that a substantially correct view has been taken of the various energy terms involved. A critical increment of 40,000 cals. means that the dianthracene molecule should absorb at $707\mu\mu$, approximately, or just at the red end of the visible, provided the simple one quantum-one molecule relation holds good. The measurements carried out in this connection are given in the next section.

Absorption of Dianthracene in Phenetole, and the Photo-depolymerization of Dianthracene

The calculated position of the absorption band involved in the depolymerization, as already stated, is $707\mu\mu$, approximately. The difficulties of measuring an absorption in this region, and the possibility (though somewhat remote) of either a multiple or submultiple being effective led to an examination first in the region $353\mu\mu$. The absorption of phenetole, even as a thin film between two quartz plates is, however, so great at this point that with the amount of dianthracene present—its solubility is much smaller than is that of anthracene—it was evident that the absorption of dianthracene, if any, would not be detected. For the purpose of this measurement, therefore, absolute alcohol was employed in place of phenetole. Four bands were observed, namely at 375, 355, 338 and $325\mu\mu$. These bands appear also in the anthracene spectrum under similar conditions. None of these, therefore, is typical of dianthracene as distinct from anthracene.

An examination in the infra-red region from 0.8μ to 3.0μ of a solution of dianthracene in phenetole showed the solvent bands alone. Dianthra-

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[10] Compare Weigert, *Ber.*, **42,** 852 (1909).

cene does not absorb, therefore, at 1.4μ or 2.8μ (multiples of 707μμ). There still remained the question of detecting absorption at 707μμ itself. An attempt with a Nutting photometer led to no definite conclusions, probably due to the fact that even a saturated solution contains too little dianthracene. Using a copper arc as a source of light and exposing a panchromatic plate for half an hour, two lines were isolated at 793μμ and 809μμ. A comparison of anthracene and dianthracene solutions in phenetole gave no apparent absorption by the latter at 707μμ. The same negative result was found on using a strontium arc (strontium chloride in a cored carbon electrode) which possesses a strong line at 707μμ.

If absorption does actually occur at 707μμ, anthracene should be formed and this should bring into existence an absorption band at 1.8μ previously found to be characteristic of this body. As absorption at this point is used as an analytical means for the detection of anthracene in the photochemical experiments to be recorded, the following data obtained for a saturated solution of anthracene in phenetole (3 g. in 100 cc.) under the conditions of measurement to which Fig. 1 refers, may be given.

Percentage transmission at 1.8μ of phenetole (0.2138 cm.)	=58.5
Percentage transmission at 1.8μ of a saturated anthracene solution	=56.3
∴ Decrease in percentage transmission due to anthracene	= 2.2

To find whether anthracene was produced photochemically by the exposure of a dianthracene solution to radiation from a Nernst filament from which a narrow spectral region containing the wave length 707μμ had been isolated by means of the spectrometer—incidentally with considerable loss in intensity—the following experiment was carried out.

Two cells of thicknesses 0.0612 and 0.275 cm. were filled with a solution of dianthracene in phenetole and the percentage transmissions at 1.8μ and 2.0μ were observed. The solution being stationary in the cell, time was allowed to elapse in order that the temperature of the exposed solution might return to that of the room before confirmatory readings were taken. The thicker cell was then exposed to the practically monochromatic radiation at 707μμ furnished by means of the spectrometer. After some hours a further examination of the absorption of the cells at 1.8μ and 2.0μ was made. It was found that the absorption at 1.8μ had increased while that at 2.0μ remained constant. Further the amount of this increase was approximately proportional to the time of exposure. Before concluding, however, that we are here dealing with a true photochemical reaction it is necessary to show that the thermal decomposition due to rise in temperature on exposure is negligible. The rise in temperature observed was less than 2°; that is, the temperature did not depart much from that of the room. Even at 35° the thermal reaction is exceedingly slow, for the velocity constant of depolymerization at 35° can be shown, on applying the Arrhenius expression to the data of Luther and Weigert, to be of the order 10^{-10}. Thus assuming that the exposed cell is at 35° (that is, that the temperature has risen more than 10°) for a period of 60 hours, we have: $k = 1/t \log C_0/C_t$, where C_0 is initial concentration and C_t that at time t. It follows that at 35°, $10^{-10} = \frac{1}{3600} \log C_0/C_t$. That is, C_0 does not differ from C_t by a sensible amount, or in other words there is no detectable change in the amount of dianthracene present due to the increase in temperature which accompanies the exposure to the radiation. Any changes in concentration observed are due, therefore, to the photochemical effect of the 707$\mu\mu$ radiation. Table I summarizes the results obtained.

TABLE I
SUMMARY OF RESULTS

Percentage transmission at 1.8μ	58.4	58.0	57.5	56.8	56.4
Time of exposure to 707$\mu\mu$, hours	..	12.25	22.25	45.25	56.75
Decrease in the percentage transmission	..	0.4	0.9	1.6	2.0

The first pair of results was obtained by using the same solution with progressive exposure. The second pair was obtained using a freshly prepared solution in each case.

It is evident from the data just given that a true photochemical depolymerization had taken place. It is necessary, however, to point out that the numerical values given in the last row cannot be compared directly with any readings obtained in the earlier absorption measurements to which Fig. 1 refers. The values in Table I indicate an apparently greater degree of conversion than actually can have taken place when we recall the very low solubility of dianthracene itself. In the former measurements in which a solution of anthracene was compared with phenetole itself the maximum decrease in percentage transmission amounted to 2.2 at 1.8μ. In the photochemical experiment this limit appears to have been almost reached. Longer exposure would no doubt have exceeded it. The discrepancy is only apparent, however, arising from the fact that in the photochemical case the systems examined by the absorption method consist of a thin cell (unexposed) containing dianthracene alone in phenetole against which is compared a thicker cell (the actual photochemical cell) containing dianthracene together with some anthracene in phenetole.

That the photochemical depolymerization is brought about by absorption of radiation in the region of 707$\mu\mu$ alone was demonstrated further by repeating the experiment using radiation at 800$\mu\mu$ and 600$\mu\mu$, respectively. The light not being entirely monochromatic and the absorbing power of dianthracene presumably extending over a region around 707$\mu\mu$, some anthracene would be expected to be formed by exposure to the regions 800 and 600$\mu\mu$, but as the results show, the rate of formation is much slower than that at 707$\mu\mu$ itself.

With light at 800$\mu\mu$ the following results were obtained.

Percentage transmission at 1.8μ	58.5	58.3	58.0
Time of exposure to 800$\mu\mu$, hours	..	19	41.25
Decrease in percentage transmission	..	0.2	0.5

With light at 600$\mu\mu$ the following results were obtained.

Percentage transmission at 1.8μ	58.4	58.1	57.7
Time of exposure to 800$\mu\mu$, hours	..	23.5	53
Decrease in percentage transmission	..	0.3	0.7

The results obtained at the three spectral regions, respectively, are shown graphically in Fig. 2.

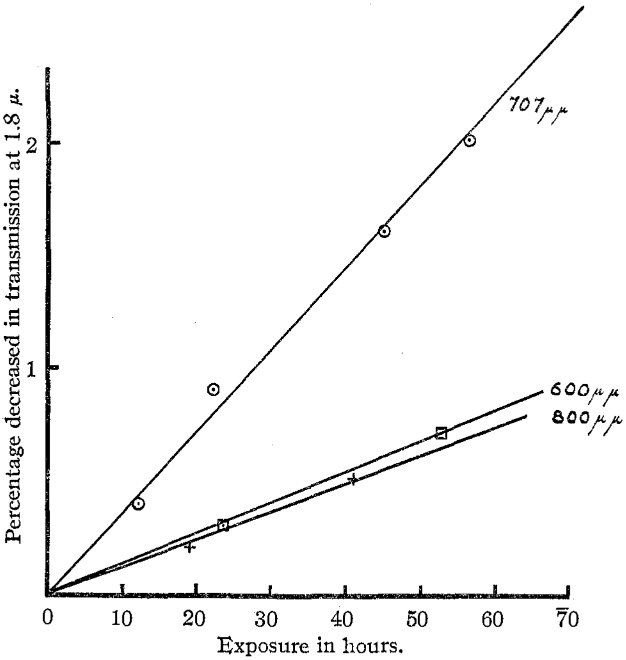

Fig. 2.

It may be mentioned that this is the first time that dianthracene has been photochemically depolymerized; hitherto, depolymerization has always been carried out thermally. The observations are a confirmation of a quantum treatment of thermal change.

One other point is possibly worthy of note. Assuming the integral relationship of band position due to Baly and Henri to be true, the position 707$\mu\mu$ is again confirmed. Thus, Henri gives the infra-red fundamental frequency of anthracene as 42×10^{12}. The two bands in the blue region at 445$\mu\mu$ and 475$\mu\mu$, that is, at frequencies 674×10^{12} and 632×10^{12}, are separated by 42×10^{12}, while the difference between the anthracene frequency 674×10^{12} and the frequency 424×10^{12}, corresponding to the wave length 707$\mu\mu$ attributed to dianthracene, is 250×10^{12}, which in turn is almost exactly six times the fundamental frequency 42×10^{12}, again indicating the integral relationship.

Summary

1. The anthracene-dianthracene system has been examined from the point of view of the radiation hypothesis of thermal change.

2. The photo-polymerization of anthracene is known to be effected by light belonging to the blue-violet region of the spectrum. Corresponding thereto, two bands at 445$\mu\mu$ and 475$\mu\mu$, respectively, have been found in the absorption spectrum of anthracene in phenetole in this region. It is concluded, in agreement with several other workers, that the fluorescence of the anthracene-dianthracene system is due to the anthracene molecule, the fluorescence being a return of an activated molecule to the normal state.

3. The absorption of anthracene in phenetole in the infra-red region has been investigated from 0.8μ to 3.8μ. Over this range anthracene exhibits only one band, at 1.8μ. From a comparison of the spectroscopic data it is concluded that in the photo-polymerization of anthracene, a single molecule is activated by absorption of blue light and then proceeds to react with an unactivated molecule to form the polymer.

4. The critical increment of dianthracene, in respect to thermal depolymerization, is shown by two methods, (*a*) from the heat effect coupled with the energy of activation of anthracene, (*b*) from the temperature coefficient of the depolymerization thermal process itself, to be 40,000 cals. in round numbers per mole. This requires that dianthracene should absorb at 707$\mu\mu$, approximately.

5. Although actual absorption at 707$\mu\mu$ has not as yet been observed by the methods employed, it has been found possible to bring about the *photo-depolymerization* of dianthracene by exposure to radiation of wave length 707$\mu\mu$. Much smaller effects are produced at 800$\mu\mu$ and at 600$\mu\mu$, respectively.

6. Dianthracene does not exhibit any absorption bands in the ultraviolet other than those exhibited by anthracene. Neither does it show absorption in the region 475–445$\mu\mu$. In the infra-red region dianthracene does not exhibit any detectable absorption over the range 0.8μ to 3.0μ.

7. The various inter-relationships found are in agreement with a quantum treatment of thermal chemical change.

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