25,530 cm.$^{-1}$ and an overlapping one of high intensity with the first strong band at 27,910 cm.$^{-1}$. Analogous separations of about 800, 1200 and 1600 cm.$^{-1}$ are evident in the members of each of the two groups. Farther in the ultraviolet is a very intense band with maximum at 40,250 cm.$^{-1}$.

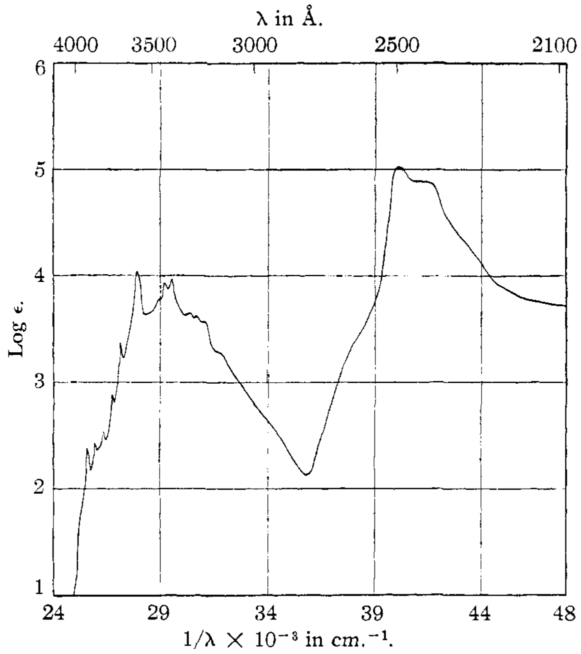

Fig. 1.

The spectrum has certain similarities to those of condensed ring compounds such as naphthalene and fluorene and this relationship would give further evidence in support of the structure of the compound as given by Lothrop.

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Purification of Anthracene

BY O. C. DERMER AND JACK KING

The observations of Clar[1] and Bachmann and Kloetzel[2] on the ease of formation and dissociation of maleic anhydride adducts of anthracenes led us to investigate the purification of anthracene itself by way of the Diels–Alder reaction. This has been discussed recently by Polyakova,[3] but his procedure is complicated by his desire to recover maleic anhydride.

Thirty-five grams of technical anthracene (purity about 80%) and 62 g. of maleic anhydride (200% excess) were added to 700 ml. of benzene and the solution refluxed for ninety minutes. The solid anthracene-9,10-*endo*-α,β-succinic anhydride that separated from the cooled mixture was recrystallized twice from aqueous acetone; yield, 29 g. (67%).

Pyrolysis of this compound by itself proved unsatisfactory, but when it was ground with 40 g. of soda lime and heated strongly in a porcelain dish covered with an inverted funnel and a receiver, anthracene having a slight yellow tinge sublimed out. This was collected and recrystallized twice from toluene. Fifteen grams (80% for this step only) of colorless, highly fluorescent anthracene, m. p. 217° (cor.), was obtained.

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(1) Clar, *Ber.*, **64**, 2194 (1931).

(2) Bachmann and Kloetzel, THIS JOURNAL, **60**, 481 (1938).

(3) Polyakova, *Org. Chem. Ind.* (U. S. S. R.), **7**, 305 (1940); *Chemical Abstracts*, **35**, 4008 (1941).

The Dissociation of Tetraphenylhydrazine and its Derivatives

BY GILBERT N. LEWIS AND DAVID LIPKIN

In a recent study by Cain and Wiselogle[1] of the rate of reaction between tetraphenylhydrazine and nitric oxide, it was shown that the rate-determining step is the dissociation of the hydrazine into two diphenylnitrogen radicals. For this process they obtain 30 kcal. as the heat of activation.

In contrast with this high energy of activation for the dissociation process, they point out that, by the ordinary method of calculating bond energies from thermochemical data, the heat of dissociation of hydrazine itself is only 20 kcal.[2] They agree with Wieland[3] that the substitution of phenyl groups would greatly reduce this figure. A large heat of activation for the dissociation and a small heat of dissociation would imply a high activation energy also for the reverse process: the formation of tetraphenylhydrazine from two molecules of diphenylnitrogen.[4] In the analogous reaction by which a molecule of hexaphenylethane is formed from two molecules of triphenylmethyl, activation is required amounting to 6–8 kcal.[5] The existence of such a heat of activation for the recombination of nitrogen free radicals would be of much interest in connection with the theories recently set forth by Lewis and Seaborg.[6]

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(1) Cain and Wiselogle, THIS JOURNAL, **62**, 1163 (1940).

(2) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 2nd ed., 1940.

(3) Wieland, "Die Hydrazine," Ferdinand Enke, Stuttgart, 1913.

(4) See also a discussion of this question, *Chem. Soc. London Ann. Repts.*, **37**, 268 (1940).

(5) Ziegler, Orth and Weber, *Ann.*, **504**, 131 (1933).

(6) Lewis and Seaborg, THIS JOURNAL, **61**, 1886 (1939).

In a forthcoming paper we shall show how it is possible to prepare numerous free radicals by ultraviolet illumination of the parent substances when dissolved in a rigid solvent. In this way we have prepared diphenylnitrogen by illuminating tetraphenylhydrazine and other substances containing this group. In a solvent which is rigid at 90°K. (but becomes fluid at about 100°K.) we find that the radical can be formed, and kept for a week or more, at the temperature of liquid air. However, the radicals recombine instantly when the temperature is raised about 10°. So rapid a reaction at 100°K. is incompatible with a heat of activation of more than about 1 kcal.

In view of the wide disparity between this result and that predicted by Cain and Wiselogle,[1] we are forced to question their estimate of the heat of dissociation of hydrazine and its aryl derivatives. In the first place, we doubt the validity of the assumption that the heat of dissociation in a case like this can be immediately determined from the so-called bond energy. Thus the bond energy of O–O is taken to be 35 kcal.,[2] but if we use the heat of formation of the OH radical chosen by Taube and Bray,[7] and the accepted value for the heat of formation of H_2O_2, the heat of dissociation of hydrogen peroxide into hydroxyl radicals is between 5 and 10 kcal. higher than the 35 kcal. assigned as bond energy. Moreover, we believe that with a heat of dissociation of only 20 kcal., hydrazine at room temperature would be an even more reactive substance than it actually is.

In the second place, we believe it not unlikely that the heat of dissociation of tetraphenylhydrazine may be as great as, or greater than, that of hydrazine itself, for the following reasons: in hexaphenylethane there are no important resonances except of the Kekulé type, while in the radicals which are produced by its dissociation there are many new opportunities for resonance. On the other hand, in the case of tetraphenylhydrazine there exist the important kinds of resonance which may be said to distribute the basic properties of the lone pair on each nitrogen atom among the several ortho and para positions in the rings. Yet, in this case also, the number of important resonance forms in the radicals presumably exceeds the number in the undissociated molecule, so that from this point of view alone we should expect the heat of dissociation of tetraphenylhydrazine to be less than that of hydrazine.

There is, however, another important factor to which perhaps too little attention has been paid. While the two nitrogens of hydrazine have no formal charge, they are both negative in the sense in which such terms are used in consideration of dipoles. The coulombic effect of these negative charges is to diminish the energy required to dissociate the molecule. Any diminution of these charges will tend, therefore, to strengthen the N–N bond. Phenyl groups have this effect. The difference in basic strength between aromatic and aliphatic amines is evidence of the partial withdrawal of the lone pairs of the nitrogen atoms into the benzene ring. We believe therefore that, owing to this loss of coulombic repulsion, the heat of dissociation of tetraphenylhydrazine is high and presumably equal to the 30 kcal. found for the heat of activation.

If this view is correct, then the substitution of one or more basic radicals in ortho or para positions of tetraphenylhydrazine would drive the electron pairs toward the nitrogen atoms and thus diminish the strength of the N–N bond. In fact, Wieland[3,8] found that the introduction of four para methoxy groups led to appreciable dissociation of the hydrazine, while four dimethylamino groups led to a dissociation of 10% at room temperature in benzene solution.

On the other hand, a similar substitution of acid groups should strengthen the N–N bond, and Wieland found that one para nitro group diminished the dissociation while two such groups diminished it still more. It would be interesting to continue this series further as additional nitro groups are substituted in the para and ortho positions. It might be possible to find a point at which further substitutions would produce increasing dissociation: namely, at the point where the nitrogens cease to have negative and begin to have positive charges.

If we apply a similar argument to hexaphenylethane we must conclude that the two central carbon atoms are nearly neutral, for every known substitution increases the dissociation.

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[7] Taube and Bray, THIS JOURNAL, **62**, 3357 (1940).

[8] Wieland, *Ber.*, **48**, 1078 (1915).