

whose most reactive centers are sterically blocked, attributes which should favor simple electron transfer rather than bond formation. A deep blue solution of K^+DPA^- was easily prepared by treating a slight excess of DPA with potassium in boiling THF.^{7,8} Unfortunately, our attempts to prepare DPA^+ and DPA^{+2} were fruitless.⁹

We then used the 9,10-dichloride of DPA ($DPACl_2$) as a potential source of DPA^{+2} . Indeed, it reacted instantly with K^+DPA^- giving a bright chemiluminescence which was visually identified as the fluorescence of DPA. The luminescent reaction is probably not a simple bimolecular process but is possibly termolecular: $DPACl_2 + 2DPA^- \rightarrow 2DPA + DPA^* + 2Cl^-$. The K^+DPA^- may be aggregated at this concentration (0.04 M) in THF. We also found chemiluminescence during the reaction of sodium naphthalene with $DPACl_2$ (THF solution). The general framework of recombination luminescence is still capable of providing an explanation at this point. Phosphorescent emission, commonly associated with this process, would not occur in fluid solution. Fluorescence might, however, result from triplet-triplet annihilation.¹⁰

Further investigation of the reactions of K^+DPA^- with various electron acceptors has shown that chemiluminescence in these systems is a more general phenomenon than had been heretofore supposed. The rapid luminescent reaction of K^+DPA^- with Cl_2 may be rationalized by assuming the intermediate formation of $DPACl_2$. However, bright chemiluminescence also accompanies the reaction of K^+DPA^- with benzoyl peroxide, oxalyl chloride, mercuric chloride, and aluminum chloride, cases in which the intermediacy of reducible, oxidized DPA derivatives is quite unlikely. We measured the emission spectrum of the benzoyl peroxide reaction and found it to be the same as the fluorescence spectrum of DPA (both in dioxane). The sole nonacidic product of this reaction is DPA.¹¹ Thus it appears that the reaction of a good oxidizing agent (where neither it nor its reduction product is a quencher) with DPA^- is capable of producing singlet excited DPA. The available data do not implicate the triplet. The chemiluminescent process is not limited to hydrocarbon ions and we expect that radical anions derived from various fluorescent species will exhibit this behavior. For example, the green solution (ether) obtained from the reaction of sodium with N-methylacridone, undoubtedly containing the ketyl, affords a bright chemiluminescence (visually the same as N-methylacridone fluorescence) upon reaction with benzoyl peroxide.

The luminescent reaction of DPA^- with reagents such as benzoyl peroxide cannot be explained easily within the established framework of recombination luminescence. We postulate that the luminescent reaction

(7) Cf. R. Gerdil and E. A. C. Lucken, *Helv. Chim. Acta*, **44**, 1966 (1961).

(8) Tetrahydrofuran was distilled from the sodium ketyl of benzophenone. All reactions were run under nitrogen.

(9) We abandoned these experiments upon learning from Professor Harold Hart of Michigan State University that his experiments had indicated that internal cyclization occurred readily in cations derived from DPA. We are grateful to him for informing us of his results and for permission to quote them prior to publication.

(10) C. A. Parker and C. G. Hatchard, *Proc. Chem. Soc.*, 147 (1962); *Proc. Roy. Soc. (London)*, **269**, 570 (1962).

(11) The reaction was carried out in ether. After evaporation of the solvent (N_2), the residue was treated with NaOH-EtOH (3 hr., 25°). The infrared spectrum of the nonacidic, crystalline product was identical with that of DPA.

involves *only the transfer of an electron from DPA^- to the acceptor*. One possible explanation for the chemiluminescence is that this reaction (which could proceed by electron tunneling) liberates energy within a small volume in a time which is very short compared to that required for its escape as heat to the medium at large. This energy may be accepted by a molecule within the solvent cage which has an accessible electronic state. The question of the relative nuclear geometries of R , R^- , and R^* and the importance of any differences in bond lengths may be raised at this point. Clearly, if $R^- \rightarrow R + e^-$ is to be followed quickly by $R \rightarrow R^*$, the geometry of R must be such that it can readily accept the energy. We do not feel that much can be said at this point other than to note that both R^- and R^* would be expected to have longer bond lengths than R and that they may be closer in geometry to each other than they are to R . An alternative model may be based on simple orbital theory. In this picture the effective result of the electron-transfer process is that the electron which is transferred is one from the highest bonding level of the radical ion R^- , and thus directly generates an excited state of R .

We wish to point out our disagreement with a view that has appeared frequently in the literature. A reaction is *not* likely to generate a product in an excited electronic state merely because it provides sufficient energy to do so. In a reaction which involves bond formation and/or cleavage, the energy is not likely to be liberated as fast as it is in a reaction involving only the transfer of an electron. Instead, the energy is likely to be liberated relatively slowly and absorbed as bond vibrations in several molecules as the transition state is traversed.

We intend to investigate other reactions involving electron transfer and we hope to extend the generality of our observations.

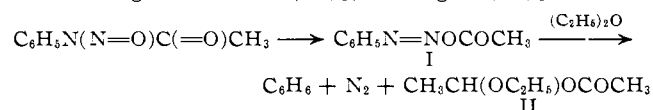
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Decomposition Reactions of N-Nitrosoacetanilide¹

Sir:

It is well established that N-nitrosoacetanilide rearranges to phenyldiazo acetate (I). The mechanisms by which I reacts have been the subject of considerable investigation and controversy.² It is the purpose of this report to describe experiments which have a bearing on this issue.

Decomposition of I in diethyl ether proceeds smoothly at 25° to give benzene (52%), nitrogen (59%), and 1-



ethoxyethyl acetate (II, 22%).³ In another experiment, treatment of the reaction mixture with 2,4-dinitrophenylhydrazine afforded a 50% yield of acetal-

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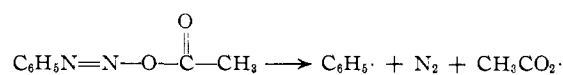
(2) (a) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 153-159; (b) E. L. Eliel, M. Eberhardt, O. Simamura, and S. Meyerson, *Tetrahedron Letters*, **No. 17**, 749 (1962); (c) D. H. Hey and M. J. Perkins, *ibid.*, **No. 7**, 445 (1963).

(3) The benzene yields were determined by ultraviolet analysis. The structure assignment of II rests on infrared and n.m.r. analysis and its formation of acetaldehyde 2,4-dinitrophenylhydrazone.

dehyde 2,4-dinitrophenylhydrazone. Reaction in ether containing an equimolar amount of acrylonitrile changed the time for 40% nitrogen evolution from 62 min. to 106 min. The yield of benzene was reduced to 23%. No II could be isolated, although a small amount may have been formed. When dioxane was used in place of ether, benzene (46%), nitrogen (58%), and 1-dioxanyl acetate (22%) were formed. Treatment of another reaction mixture with 2,4-dinitrophenylhydrazine gave glyoxal 2,4-dinitrophenylhydrazone (36%).

N-Nitrosoacetanilide reacted in benzene to give 87% nitrogen, <1% carbon dioxide, and 72% biphenyl.⁴ Reaction under the same conditions except for the addition of a 10-mole excess of acrylonitrile increased the time required for 40% nitrogen evolution from ca. 90 to 290 min. No biphenyl was formed under these conditions. Decomposition in benzene containing a 10-mole excess of styrene increased the time for 40% nitrogen evolution to 146 min. Again biphenyl formation was completely suppressed. Finally, decomposition in the presence of a 10-mole excess of 2,6-di-*t*-butyl-*p*-cresol had very little effect on the rate of nitrogen evolution, but again no biphenyl was formed.

Previous mechanistic proposals for the reactions of I have involved rapid homolysis^{2a,b,5} after a slow rear-



angement of the N-nitroso compound. In aromatic solvents it has been suggested that further reaction of phenyl radicals and acetoxy radicals yields biphenyls and acetic acid. Many workers have recognized that the postulation of acetoxy radical formation without subsequent carbon dioxide formation requires very rapid reaction of the acetoxy radicals. In essence this anomaly has been rationalized by suggesting that biaryl formation involves a "cage reaction."^{2b,5}

The results reported here do not support this concept. The obtention of II and dioxanyl acetate is not in agreement with a simple dissociation mechanism.

(4) These yields are comparable to those reported by many investigators.

(5) R. Huisgen and G. Horeld, *Ann.*, **562**, 137 (1949).

Such a mechanism requires that a phenyl radical abstract an α -hydrogen from ether to give an α -alkoxy radical which then combines with an acetoxy radical. All of this must occur before the acetoxy radical can decarboxylate.⁶ The formation of II and dioxanyl acetate is readily explained by a mechanism involving induced decomposition of I. Attack by an α -alkoxy radical on I to give ester, nitrogen, and a phenyl radical is a very reasonable means of forming ester and perpetuating a chain reaction involving phenyl radicals. This mechanism readily explains the diminution in benzene yield in the presence of acrylonitrile.⁷ The effect of inhibitors on biphenyl yields is particularly striking and demonstrates that the course of the reaction is completely modified by these substances. In this connection it is important to note that nitrogen yields were not affected by the inhibitors. It seems reasonable to conclude that phenyl radicals and/or phenylcyclohexadienyl radicals, their addition product to benzene, are trapped before biphenyl formation can occur. These results certainly suggest that free phenyl radicals are involved in biaryl formation. A "cage reaction" should not be affected by an inhibitor.⁸ These observations suggest that the reaction of I in benzene involves induced decomposition rather than a "cage reaction."⁹ Clearly further work is required, and such is in progress.

(6) No more than 1% of carbon dioxide is formed during the decomposition in ethers.

(7) It is reasonable to assume that the monomer competes with the ether for phenyl radicals.

(8) It should be emphasized that two of the inhibitors decreased the rate of nitrogen evolution; thus it seems safe to conclude that the monomers are not reacting with N-nitrosoacetanilide or I. If this occurred, nitrogen formation would necessarily have to be faster than in the absence of inhibitor.

(9) Another piece of evidence which mitigates against a "cage reaction" and which has not been noted in this context is the essential absence of true "cage" product, phenyl acetate. Indeed, in a very careful investigation, T. Inukai, K. Kimura, O. Simamura, and T. Suehiro [*Bull. Chem. Soc. Japan*, **35**, 129 (1962)] showed that decomposition of methyl N-nitroso-*p*-acetamidobenz[C¹⁴]oate in benzene yielded only 0.046% of methyl 4-acetoxybenzoate.

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BOOK REVIEWS

Chemical Analysis. Volume XIII. Alternating Current Polarography and Tensammetry. By B. BREYER and H. H. BAUER, School of Agriculture, Section of Agricultural Chemistry, The University of Sidney, Sidney, N.S.W., Australia. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1963. 228 pp. 15.5 × 23.5 cm. Price, \$12.00.

Despite their longtime recognition as basically valuable approaches to the study of moderately fast electrode processes, alternating current voltammetry (including polarography) and tensammetry, as distinct from bridge impedance methods, have been rather slow to command very widespread experimental interest among workers in this country. A good portion of this neglect might be ascribed as much to the slow development of a corpus of theory which could take acceptable account of the complex periodic relationships at the electrode surface, as to the experimental uncertainties and awkwardness of early instrumentation. Consolidation and extension of basic theory as well as recent improvements in experimental accuracy and convenience which have resulted from the successful use of new and improved types of instrumentation, such as operational amplifier circuitry, "lock-in" type phase discriminating ampli-

fiers, wave analyzers, etc., make it seem increasingly likely that a.c. voltammetry will elicit greater attention as an important investigational tool. Such expectation receives added strength with the appearance of this book by Breyer and Bauer which constitutes the first monograph review in this field. The book brings into long-needed focus a wide scattering of work which ranges over a twenty-two year period from the first measurements by Müller and co-workers around 1938, and it thus incorporates a good deal of the valuable exploratory effort of the early Australian school which appeared in journals that remain largely inaccessible to the average worker. Some 90 pages of the (228-page) text are devoted to introductory material and a review treatment of theory, including faradaic rectification, with some mention included of square-wave and radiofrequency polarography. Instrumentation is covered in the chapter following, and, on reading this, one is struck by the somewhat arresting fact that, except for the Mervyn-Harwell Square Wave Polarograph, most if not all of the classical a.c. polarographic instrumentation described in this chapter are of Japanese manufacture. Chapter 4 provides an extensive outline discussion of available information, much of which is qualitative, bearing on inorganic and organic applications of a.c. polarography, as well as a review of the