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THE KINETICS AND LINEAR FREE ENERGY CORRELATION OF THE ALCOHOLYSES OF SOME N-AROYL-N'-PHENYL DIIMIDES AND N-BENZOYL-N'-ARYL DIIMIDES

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Sir:

A few years ago, we reported that the alcoholysis of N-Benoyl-N'-phenyldiimide led to the formation of phenyl radicals.[2] Thus this reaction sequence was indeed unique, since it was a heterolysis, which was followed by a homolysis in a polar media.

Whereas, on the one hand, the homolytic nature of the reaction was quite well substantiated, for example, radical phenylation of benzene and nitrobenzene, phenyl radical abstractions of hydrogen from alcohols and chlorine from carbon tetrachloride; and lastly phenyl radical initiation of polymerization were reported. On the other hand, the heterolytic nature of the sequence was only based on the production of moderately high yields of methyl benzoate, when the reaction was carried out in methanol. Also prior to our study, Leffler and Bond[3] had reported that the decomposition of a closely related series of substituted N, N'-dibenzoyl diimides in ethanol, also produced radicals, but they concluded that as opposed to the reaction undergoing a heterolysis in the initial stages, that they were dealing with a homolytic reaction which was sensitive to polar medium and polar substituents.

Thus, in order to illustrate more dramatically the heterolytic nature of the decomposition of of N-Benzoyl-N'-Phenyl diimide, we have investigated, and wish to report the kinetic study of two series of disubstituted diimides, A and B, in 70% aqueous ethanol, 0.1 M potassium chloride at 30.0 °C.[4] See Table I.

Table I

Series A

N-Aroyl-N'-Phenyl Diimide[5]	$K_{ave.} \times 10^5$ sec.$^{-1}$[6]
N-Benzoyl-N'-Phenyl Diimide	5.53 ± 0.20
N-p-Toluoyl-N'-Phenyl Diimide	2.16 ± 0.10
N-p-Chlorobenzoyl-N'-Phenyl Diimide	31.50 ± 0.50
N-p-Methoxybenzoyl-N'-Phenyl Diimide	1.18 ± 0.04

Series B

N-Benzoyl-N'-Aryl Diimide[5]	$K_{ave.} \cdot 10^5$ sec.$^{-1}$[6]
N-Benzoyl-N'-Phenyl Diimide	5.53 ± 0.20
N-Benzoyl-N'-p-Tolyl Diimide	2.68 ± 0.10
N-Benzoyl-N'-p-Chlorophenyl Diimide	10.20 ± 0.30
N-Benzoyl-N'-p-Nitrophenyl Diimide	78.30 ± 3.30
N-Benzoyl-N'-m-Nitrophenyl Diimide	50.30 ± 2.30

Both series A and B satisfy the Hammett relationship when plots of log $K_{ave.}$ versus σ were made, where σ is standard sigma constants. The rho values for series A and B were +2.75 and +1.43 respectively. We believe that the magnitude and sign of these rho values strongly signify a nucleophilic attack and subsequent displacement at the carbonyl group. The positive sign of these values may be compared with the rho value of +1.92 obtained by Branch and Nixon[7] for the ethanolysis of a series of substituted benzoyl chlorides. The facile alcoholysis of these compounds tends to indicate that the phenyl azo anion and/or phenyl diimide are fairly good leaving groups.

The fact that series A is more sensitive to the effect of the substituent than series B is consistant with the substituent being closer to thereaction site. Also from a comparison of the rho values of series A and B, one can get a measure of the transmitting efficiency of -N=N- moiety, where the transmitting efficiency,[8] ε, is equal to $\frac{\rho \text{ Series B}}{\rho \text{ Series A}}$ is 0.52. This value is to be compared with a value of 0.48 and 0.50 for trans and cis C=C[8], respectively.

The above indicates that the transmitting efficiency of the azo linkage is similar to that of the ethylenic linkage. We are currently exploring other systems to corroborate this.

NOTES

(1) We are pleased to acknowledge the generous support this work in part by Petroleum Research Foundation Grant 894-G1.

(2) Cohen, S. G. and J. M. Nicholson, J. Am. Chem. Soc., 86, 3892 (1964); J. Org. Chem., 30, 1162 (1965).

(3) Leffler, J. E. and W. B. Bond, J. Am. Chem. Soc., 78, 335 (1956).

(4) The kinetics were carried out on a Sargent Recording Polarograph Model XXI equipped with a thermostated H cell. These disubstituted diimide gave a well defined reduction wave, whose diffusion current, id, was directly proportional to the concentration of the substrate. Caromel electrode was used as the standard reference, and the dropping mercury electrode was the working electrode.

(5) The elemental analyses of new compounds agreed well with calculations, and their infrared and ultraviolet spectra were consistent with the assigned structures.

(6) The specific rate constants are an average of two determinations. The initial concentration of the substrate was 10^{-3}M.

(7) Branch, G. E. K., and Nixon, A. C., J. Am. Chem. Soc., 58, 2499 (1936).

(8) Miller, S. I., Symposium on Linear Free Energy Correlations, pp. 45, October 1964 and reference therein.