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KINETIC STUDIES OF BROMINE ADDITION TO OLEFINS

X. THE BROMINATION OF 1,1-DIPHENYLETHYLENES

AN ASYMMETRICAL TRANSITION STATE

J.E. Dubois and W.V. Wright*
Faculté des Sciences, Laboratoire de Chimie Organique Physique
1 rue Guy de la Brosse, Paris 5e

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Until recently, the high rates of addition of halogen to phenyl substituted olefins precluded a systematic study of these reactions. Over the last few years, instrumentation (1,2) for convenient measurement of fast bromination reactions in solution has been developed in this laboratory. These techniques, previously employed to study the bromination of some substituted styrenes (3), have been used to measure the rates of bromine addition to a series of 1,1-diphenylethylenes (4), and the results are presented here.

The rate constants, listed in Table I, were measured in methanolic 0.2 M sodium bromide solutions at 25°C. These observed rate constants are therefore composite and reflect the rate of bromination by both molecular bromine and tribromide ion. While the respective rate constants for these two processes can be

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*N.A.T.O. Post-Doctoral Fellow 1965-66

evaluated by measuring the rate of addition at varying bromide ion concentrations, the composite rate constants, k_g have been used successfully for studying the effect of molecular structure on reactivity (5) and are so used here.

TABLE I

Bromination Rate Constants k_g measured at 25 ± 0.02°C

1,1-diphenylethylene	k_g $lmol^{-1}sec^{-1}$	n	% mean deviation
4,4'-dimethoxy	3.47×10^6	3	1.8
4-methoxy	3.77×10^5	4	4.4
4,4'-dimethyl	9.84×10^4	3	1.7
4-methyl	1.57×10^3	5	6.4
4-fluoro	1.33×10^2	5	6.6
4,4'-difluoro	1.23×10^2	4	2.2
4-chloro	4.76×10^2	6	7.7
4-bromo	3.62×10^2	5	8.8
4,4'-dichloro	1.28×10^1	5	6.6
4,4'-dibromo	1.03×10^1	3	4.2

n is the number of kinetic experiments.

In considering the effect of structure on reactivity it is customary to plot the logarithm of the measured rate constants versus the appropiate Hammett substituent constants σ (6). Applying the Hammett treatment to the present case, log k_g versus produced a curve, the p-methoxy and the p-methyl derivatives being more reactive than their Hammett σ constants would imply. In such cases a linear plot is usually obtained by the use of Brown σ^+(7) values, but for these 1,1-diphenylethylenes the constants overcorrected for resonance interactions and the plot curved downwards.

Recently Yukawa and Tsuno (8) have demonstrated that reactions involving resonance stabilization of a positive charge in which the relative importance of the resonance interaction mechanism differs from that in the two relationships defining σ and σ^+, can be handled by a linear combination of these two models. Their modified Hammett equation takes the form

$$\log k = \rho(\sigma + r\Delta\sigma_R^+) + \log k_0 \qquad \dots\dots\dots\dots\dots\dots \qquad \text{I}$$

where r is a new reaction constant indicative of the degree of resonance in the transition state and $\Delta\sigma_R^+$ corresponds to $(\sigma^+ - \sigma)$. The $\Delta\sigma_R^+$ values for well behaved meta substituents are essentially zero, and these are normally used to evaluate rho. The remaining parameter, r, can then be obtained by plotting the function $(1/\rho \log k/k_0 - \sigma)$ versus $\Delta\sigma_R^+$. In the present series, however, no meta substituted derivatives were available at the time and so equation (I) was rewritten in the form:

$$\log k = a\sigma + b\Delta\sigma_R^+ + \log k_0 \qquad \dots\dots\dots\dots\dots\dots \qquad \text{II}$$

where a and b correspond to ρ and $r\rho$ respectively. With the aid of a computer and using the experimentally determined values for k_g, equation (II) was solved for a and b on a least squares basis (9). The Yukawa-Tsuno-Hammett equation (I) for the bromination of 1,1-diphenylethylenes was then calculated to be

$$\log k_g = -3.61 \quad (\sigma + 0.415\Delta\sigma_R^+) + 5.11 \qquad \dots\dots\dots\dots\dots \qquad \text{III}$$

The good fit of the experimental points to this linear equation is shown by the correlation coefficient $(r = 0.991)$ and standard deviation $(s = 0.165)$.

The rho value is somewhat lower than that obtained for the bromination of styrenes measured under the same conditions (3) and implies less charge developement in the transition state for the bromination of these 1,1-diphenylethylenes. Of particular interest is the low value of 0.415 for r. This low value indicates reduced resonance interaction in the transition state relative to that in styrene bromination (10).

The molecule of 1,1-diphenylethylene cannot have the two phenyl rings simultaneously coplanar with the olefinic bond. Scale models show that the steric interference of the ortho hydrogens may be relieved either by equal twisting of both phenyl rings through an angle of approximately 30° or by rotation of one phenyl ring through about 60° leaving the other phenyl coplanar with the olefinic moiety as in styrene. On the basis of dipole moment data, Sutton (11) assigned an equal twisting of some 30° to both phenyl rings. Theoretical calculations involving steric repulsion energy (ortho-hydrogens) and loss of delocalization energy (through phenyl rotation) terms indicated a similar conformation to be the most stable for the molecule (12).

It is generally accepted that effective resonance interaction between a para substituted phenyl ring and an adjacent carbonium centre requires coplanarity of the aromatic π-orbitals and the empty p-orbital of the carbonium ion. The reduction in resonance interaction due to twisting through an angle θ is to a first approximation equal to $\cos^2 \theta$ (13). In the transition state of a 1,1-diphenylethylene reaction, an equal twisting of both rings through approximately 30° would result in a twenty-five percent drop in resonance for each ring. On the other hand a greater rotation of one phenyl ring through 60°, leaving the other phenyl coplanar, would produce (for the rotated phenyl) a seventy-five percent drop in resonance interaction with the carbonium centre. While the latter case is perhaps favoured by the low value obtained for the resonance parameter r, a transition state having equally twisted phenyl rings cannot be excluded.

Assuming ad hoc that bromination involves an asymmetrical transition state, the following facts might be considered to apply. In the p,p'-disubstituted 1,1-diphenylethylenes the interaction of the para-substituent in the coplanar phenyl will be measured by its Brown σ^+ constant and that of the para-substituent in the rotated phenyl by its Hammett σ constant since in the latter case little resonance will be possible. In the monosubstituted compounds the substituted phenyl ring will be the coplanar one. Brown σ^+ constants are always the more negative (or less positive) and since this is an electrophilic reaction the above conformation would minimize the energy of the transition state. Under these circumstances the rate data should follow a modified Hammett equation of the form:

$$\log k = \rho(\sigma + \sigma^+) + \log k_0 \qquad \dots\dots\dots\dots\dots\dots \text{IV}$$

This in fact was shown to be the case and a least squares calculation revealed an excellent fit ($r = 0.995$, $s = 0.047$), the slope of the line, rho, being -3.29.

These results for 1,1-diphenylethylene seem to indicate that while equal partial twisting of the phenyl rings is the least energetic conformation in the ground state, the preferred transition state for bromination is that in which one phenyl is rotated through a larger angle leaving the other coplanar with the ethylenic moiety. An extension of these considerations to the reactions of other

1,1-diphenyl sp^2 carbon systems is intended in a more detailed paper.

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