Tetrahedron Letters No.23, pp. 2539-2544, 1966. Pergamon Press Ltd.
Printed in Great Britain.

N. M. R. STUDIES OF A HYDROGEN-DEUTERIUM EXCHANGE IN CARBONIUM ION SYSTEMS

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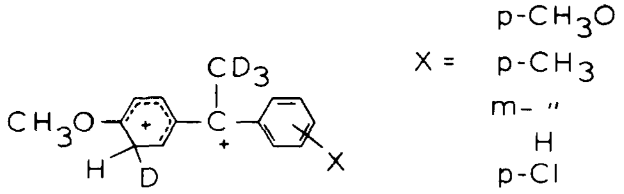
(Received 11 February 1966; in revised form 4 April 1966)

Hydrogen-deuterium exchange has been studied previously in a number of aromatic systems.[1,2,3] The data show that the reaction is a normal electrophilic substitution, accelerated by electron donating substituents, and retarded by electron withdrawing substituents. N. m. r. spectra of σ complex intermediates have also been reported,[4,5] verifying the mechanism of the substitution.

The present work is concerned with deuterium exchange in a series of cations derived from several 1,1-diarylethylenes. The effect of the substituent X on the rate of exchange suggests that exchange directly involves the cation, rather than the 1,1-diarylethylene itself. The intermediate in the former case would be a dication.



N. m. r. studies of H-D exchange in other carbonium ion systems have shown that exchange occurs very slowly,[6,7] probably due to the deactivating influence of the positive charge. The dication intermediate would be markedly destabilized by charge

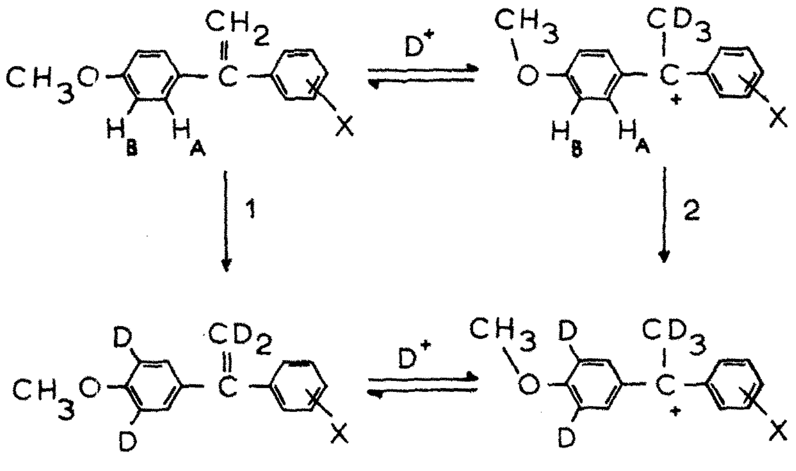


Diagram 1

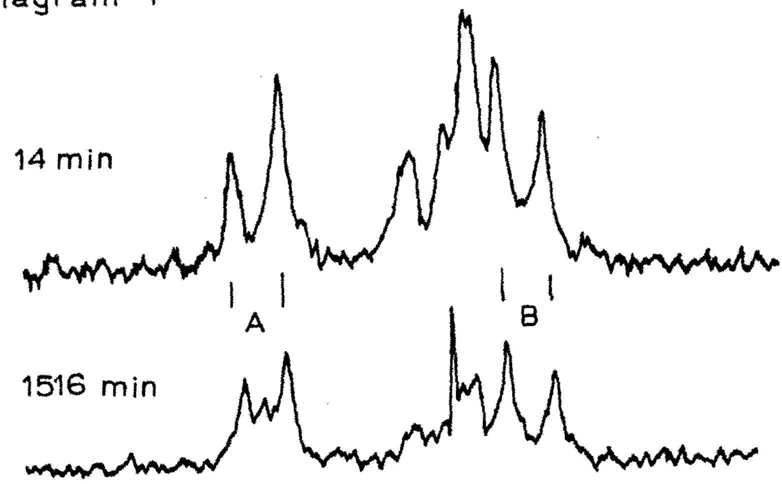


Fig 1, Aromatic absorptions at times indicated

X is m CH_3

repulsion. Recently other studies have shown that organic dications indeed are extremely unstable species.[8-10] However older work by Wizinger[11,12] showed that tetraanisyl pinacol yielded a dication in concentrated acid solution. In this case each charge possesses its own separate resonance pathway, and coulombic repulsions may be significantly reduced.[8]

Diagram 1 shows the basic system under investigation and the various possibilities for deuterium exchange. Previous work[6,7] has shown that the olefinic substrate is almost 100% converted to the diaryl cation in 96% H_2SO_4. Nevertheless, H-D exchange may take place in the small amount of olefin present in the equilibrium shown in Diagram 1. It is a question of great interest whether or not deuteration may proceed by (2) as well as (1).

N.m.r. spectra are an extremely convenient tool for studying exchanges of these types. The anisyl ring proton spectra may be approximated as an AB pattern (see Diagram 1). As deuteration progresses the resonance absorption of proton B diminishes while that of proton A is converted from a doublet to a broad singlet. The same type of behavior occurs for the other aromatic protons except at a much slower rate (depending upon the electron donating character of the substituent X). Representative spectra illustrating this effect are given in Figure 1. The extent of deuteration may be followed by integration. Five to thirteen points were taken (the tubes were thermostatted at 30.01° C. between readings). The data fit a first order rate equation quite accurately.

Table I lists the half-lives of exchange of proton B for five compounds of varying substituent. It is seen that electron donating substituents accelerate the rate of deuteration by substantial amounts. The data obey a ρ-σ^+ treatment fairly well, in which ρ is -2.6.[13] It is interesting that σ^+ parameters must be used even though resonance forms cannot be drawn in which the substituent X interacts with the complex in the remote ring.

TABLE I

Exchange Half-lives in Minutes at 30°C. for Substituted 1,1-Diarylethyl Cations

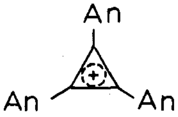
X	Anisyl Ring		x-Substituted Ring
	Proton A	B	
p-OCH_3	slow[a]	30 min.[b]	
p-CH_3	slow[a]	1200	Two protons exchange ca. 2000 min.
m-CH_3	slow[a]	5000	Three protons exchange ca. 800 min.
H	slow[a]	11,500	Very slow
p-Cl	slow[a]	12,500	Very slow

[a] No appreciable exchange in a four-week period. [b] A statistical factor of two has been applied. A temperature of ca. 38° C. was necessary, instead of the usual 30.01° C.

It is rather surprising that the tolyl protons exchange so rapidly. The terminal olefinic protons usually exchanged within a few minutes (exchange was slower in the dianisyl case).

The fact that remote substituent speed up the exchange in the anisyl ring, even though the equilibrium is shifted from olefin toward carbonium ion, suggests that pathway (2) exists. The dependence of rates of exchange on σ^+ rather than σ is not readily accommodated by exchange solely by pathway (1). In the diaryl cation electron donating substituents are thought to stabilize resonance forms involving the charge in one ring while leaving the second ring (which also has an activating substituent) susceptible to deuterium attack through the dication intermediate.

In the trianisylcyclopropenium ion,[14] exchange was essentially complete within 30 min. in 15N. D_2SO_4.



In this case the positive charge must remain primarily in the three-membered ring to maintain aromaticity. The anisyl rings are less deactivated than previous cases and exchange can occur rapidly.

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