# Acid-catalysed Hydrogen Exchange of Phenalenone

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*Summary* Evidence is presented for the mechanism of hydrogen exchange of phenalenone, involving covalent hydrate formation.

THE n.m.r. spectrum of phenalenone, after heating the compound at 120° for 3 hr in moist $CF_3CO_2D$, shows that acid-catalysed hydrogen exchange has occurred in the 2-position (Figure 1).

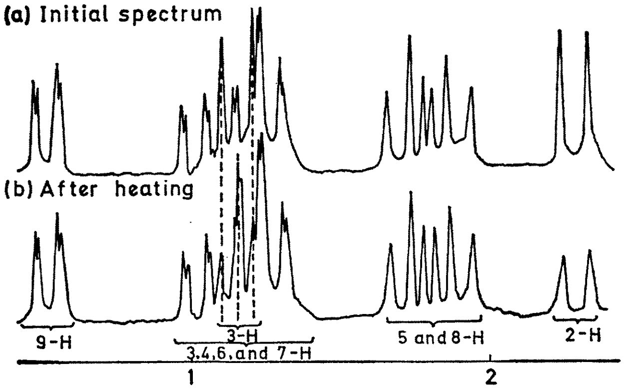


FIGURE 1. *The* 100 *MHz n.m.r. spectra of phenalenone in moist* $CF_3CO_2D$.

Dewar's PMO method,[1] which is simple to apply and has proved remarkably successful in predicting the reactivity of conjugated hydrocarbons and their heterocyclic analogues, apparently fails in this case. The reactive positions for electrophilic attack would be 2, 5, and 8, for which the relevant localisation energies ($\Delta E_\pi$) are $2{\cdot}35\beta\text{-}\alpha/3$ (0·59)[2], $2{\cdot}35\beta\text{-}\alpha/3$ (0·20)[2], and $2{\cdot}35\beta\text{-}\alpha/3$ (0·20)[2] respectively ($\alpha$ represents the coulomb integral, $\beta$ the resonance integral and the reduction factor for induction is taken as $\frac{1}{3}$).

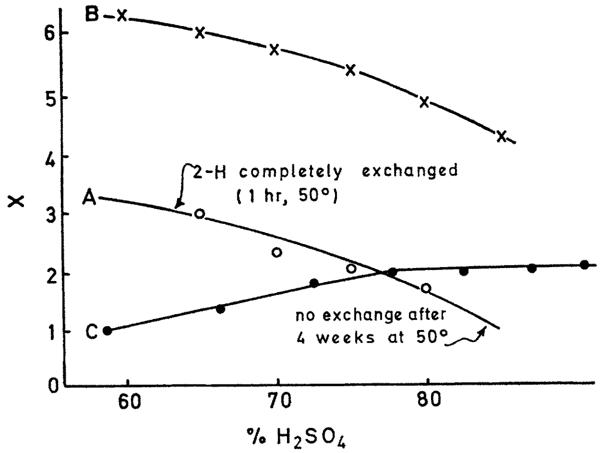
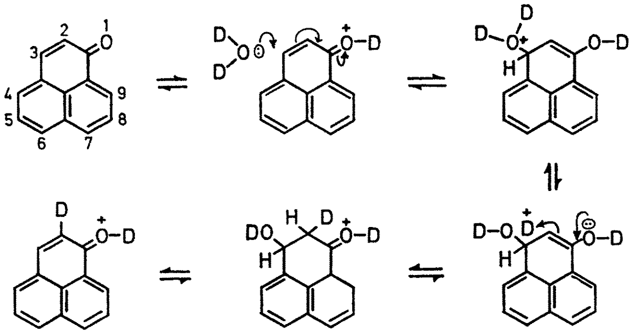


FIGURE 2. *Acidity-dependence of the rate of hydrogen exchange of phenalenone and* 4-*methylacetophenone*. A. X = *log* $k_{obs}$ *phenalenone*). B. X = *log* $a_{H_2O}$ (25°). C. X = *log* $k_{obs}$ (4-*methylacetophenone*).

Thus the heteroatom (whether protonated or not) would destabilise the transition state for 2-substitution, more than those for 5- or 8-substitution, and the theoretical prediction for electrophilic attack is $5 = 8 > 2$.

However, preliminary investigation of the rate–acidity profile in deuteriosulphuric acid at 50° (Figure 2) reveals a pattern characteristic of neither free-base nor conjugate-acid reaction.[2] Figure 2 also includes for comparison a rate profile for hydrogen exchange of the 3- and 5-positions of 4-methylacetophenone at 80°, which shows the normal free-base pattern encompassing the half-protonation point. The phenalenone profile parallels approximately the variation of log $a_{H_2O}$ in $H_2SO_4$–$H_2O$ at 25°, indicating that reaction is proceeding *via* a small concentration of the covalent hydrate.[3]

The key factor in deciding the positions of electrophilic attack is therefore the initial nucleophilic attack on the protonated form of phenalenone by a water molecule (Scheme). The reactive positions in this case would be 3, 4, 6, 7, and 9, and while the PMO calculations are ambiguous in this case, they certainly point to 3 as one of the positions more susceptible to nucleophilic attack.



SCHEME

The reaction sequence shown in the Scheme is thus appropriate for the overall reaction, in keeping with both rate–acidity profiles and PMO calculations.

The $H_0$ (half-protonation) value we have measured for phenalenone of $-1{\cdot}62$ in $H_2SO_4$–$H_2O$ is in reasonable agreement with previous workers.[4] It is not a Hammett base however; its *m* value is 1·35, possibly reflecting the carbonium ion-like character of its conjugate acid (*m* is *ca.* 1·6 for olefins). Values of $-5{\cdot}88$ and 0·82 for $H_0$ (half-protonation) and *m*, respectively, were found for 4-methylacetophenone. This *m* value is quite different from our value for acetophenone (1·26),[5] but is similar to that recorded (0·73) by Moodie and Schofield[6] for the latter compound. We therefore repeated our measurement on acetophenone, and found *m* values of 0·63, 0·66, 0·70, 0·64, and 0·70 at wavelengths of 250, 293, 296, 300, and 310 nm, respectively. Our previous error arose from inadequate separation of medium and protonation effects on the u.v. spectra.

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