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Note

Microwave effect in organic reactions

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Based upon extensive analysis of the organic reactions reported in the literature, a qualitative method for the prediction of the presence or absence of specific microwave effect in organic reactions has been advanced. The specific microwave effect will be observed only if all the reactants are polar in nature. It is unlikely to be observed if the reactions involve a non-polar reactant.

Keywords: Green chemistry, Specific microwave effect, prediction method.

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Chemistry by microwaves has gained great popularity in academic and industrial research laboratories recently[1]. This can be judged by the fact that the number of publications relating the use of microwaves in organic synthesis today stands at around 2000 since the publication of first few reports in 1986. There have been many reports in the literature of organic reactions exhibiting the "specific microwave effect" (also called the athermal microwave effect) implying that the enhanced chemical yields were obtained in reduced reaction times at the same temperature under microwave irradiations as compared to thermal conditions. Although several reviews[2-12] have been published on the increasing use of microwave dielectric heating in organic reactions, there are surprisingly little reports regarding the predictability of the presence or absence of the "specific microwave effect" in organic reactions. A prediction of the aforesaid effect in organic reactions can clearly enable chemists to take maximum advantage of the microwave radiation and open up new horizons for chemical application of microwaves[13].

Results and Discussion

Thermal effect of microwaves is known to occur as a consequence of the friction that the molecular dipoles undergo while realigning themselves with the rapidly reversing electric field of the microwaves[14]. However, the thermal effect thus generated cannot explain the "specific microwave effect" as temperature is being kept constant under both the microwave as well as the thermal conditions. That is why the microwaves are thought to have the specific microwave effect and also called the purely non-thermal or athermal microwave effect. A survey of the published literature shows many claims of the observation of specific microwave effect in many organic reactions. However, it was demonstrated that in some of the investigated reactions, the reported overheating or the super-heating phenomenon of the solvents above their b.p. by a range of 13-26ºC in refluxing conditions could be responsible for the observed rate enhancements and therefore it has been argued that there was no specific microwave effect[15–17]. Similar conclusions were also drawn in some other investigations that showed that in reactions employing supports such as alumina etc, localized super-heating zones were created which could possibly lead to the observed spectacular rate accelerations[18,19]. These localized super-heatings were said to have originated due principally to the absence of intrinsic potentialities of stirring in such materials and the inhomogeneities of the electric field of the microwaves. Yet another investigation has recently dismissed the idea of "specific microwave effect" with the creation of "hot spots" measuring about 900-1000 μm and having temperatures about 100-200 K more than the bulk temperature as observed in the decomposition of H_2S over γ-Al_2O_3 and MoS_2-γ-Al_2O_3 supports[20].

Evidently, the localized selective super-heatings and the hot spots are manifestations of the temperature effect and not the "specific microwave effect" (also called the specific microwave effect). However, this argument fails to account for the reported specific microwave effect in reactions which did not include supports e.g. alumina, silica gel, clays, etc. or other possible 'rate modifiers' such as inorganic salts or phase-transfer catalysts. Attempts have also been made to correlate the observed rate accelerations with the orientation effect of the microwaves on the reactants[21] or the transition states[3]. However, contrary arguments have also been advanced that since the energy associated with a microwave photon is even less than that required for Brownian motion orientation effects cannot be responsible for the rate enhancements and that molecular effects of the microwave electric field could, paradoxically, be observed for a medium which is not heated by the action of microwave irradiation[18,19]. It is observed[3] recently that irrespective of the mechanism of its generation, the specific microwave effect was likely to be observed only if all the reactants in an organic reaction were polar in nature and that it cannot be expected to be observed if the reactants were non-polar in nature since microwaves interact only with a polar substances and not with a non-polar substances.

From the preceding discussion, it is evident that the subject of specific microwave effect is very exciting. Because of our interest in chemistry by microwaves[24], we have now looked at this research problem by making an analysis of the published literature and we report herein for the first time a qualitative method for the prediction of the presence of the absence of the specific microwave effect in organic reactions.

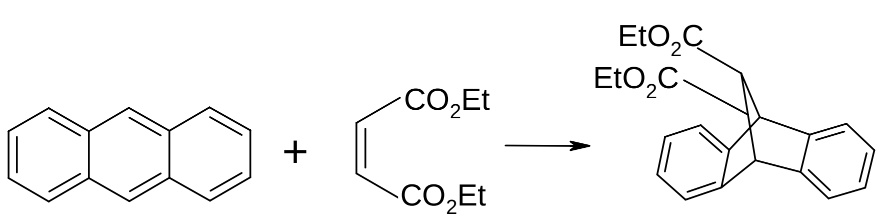
We reasoned that since solid supports such as alumina, silica gel, clays etc. can exhibit localized super-heatings, hot spots effects etc. and similarly because catalysts such as the inorganic salts or phase-transfer catalyst or ionic liquids (all of these hereafter referred to as "rate modifiers") can also show heating effect upon microwave irradiation due to conduction mechanism, it was therefore necessary that a thorough literature search was made for organic reactions which did not include any of these 'rate modifiers' and also the other 'rate modifiers' such as the polar solvents because of their interaction with microwaves they are likely to modify the microwave effect (the presence of non-polar solvents can, however, be thought to be unlikely to modify the microwave effect as these are almost transparent to microwaves). Because here the 'rate modifiers' could modify the microwave effect, it is clear that it is not possible to conclude whether the observed microwave effect was due to interaction of microwaves with the organic reactants alone or due to the presence of the 'rate modifiers' which could be responsible for enhancing the rates of reactions due to their thermal effect as mentioned earlier.

A very careful investigation of the data available in the literature[2,3] revealed mainly the two categories of reactions which showed the "specific microwave effect". First category of reactions were those which were carried out in the presence of a 'rate modifier' i.e. a polar solvent or a polar catalyst – simple or a phase-transfer catalyst or a polar support such as those mentioned above. There was the second category of reactions which did not include a 'rate modifier' i.e. a polar solvent or a polar catalyst or any other such 'rate modifier'.

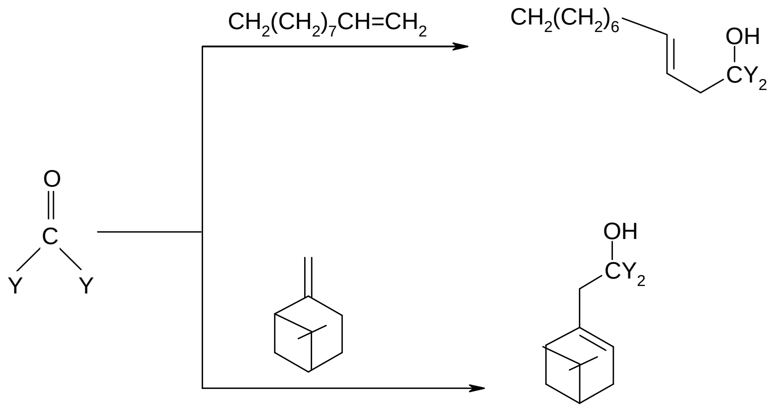
There was the third category of the reactions which did not show the specific microwave effect and also did not include a 'rate modifier' as well. For example the reactions between diethyl maleate and anthracene[22] (**Scheme I**), diethyl mesoxalate and 1-decene[23] (**Scheme II**), diethyl mesoxalate and β-pinene[23] (**Scheme II**) and the conversion of (+) citronellal to a mixture of isopulegols[23]. (**Scheme III**)

A further minute interpretation disclosed that in the second category of the reactions which showed the aforesaid effect, all of the reactants were polar in nature. However, in the third category of the reactions which did not show the said effect, one of the reactants was polar, while the other was non-polar in nature. For instance, in the reaction between diethyl maleate and anthracene, while diethyl maleate was polar, the other reactant i.e. anthracene was non-polar; in the reaction between diethyl mesoxalate and 1-decene, while the former is polar, the latter is non-polar; in the reaction between diethyl mesoxalate and β-pinene, diethyl mesoxalate is polar while β-pinene is non-polar. Similarly, in the conversion of (+) citronellal to a mixture of isopulegols, while one reaction site is polar, the other is non-polar in nature.

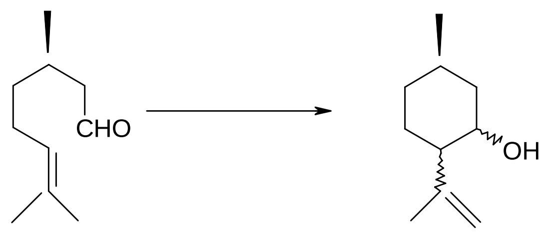
From a comparison of the second category of the reactions which showed the specific microwave effect, and the third category of reactions which did



Scheme I — Showing the reaction between diethyl maleate and anthracene in which specific microwave effect was not observed[22].



Scheme II — The reactions between (i) diethyl mesoxalate and 1-decene and (ii) diethyl mesoxlate and β-pinene both of which did not exhibit the specific microwave effect[23].



Scheme III — The conversion of (+) citronellal to a mixture of isopulegols which did not show the specific microwave effect[23].

not show the said effect, it can be reasonably concluded that the specific microwave effect is not non-existent and that specific microwave effect was likely to be exhibited by an organic reaction (not containing a 'rate modifier', of course) if all the reactants in the reaction are polar in nature and that the specific microwave effect is unlikely to be observed if one of the reactants is non-polar in nature. More examples need to be investigated in this direction to verify the validity of the method advanced herein.

Conclusion

In conclusion, based upon interpretation of the literature data, we have shown the existence of the specific microwave effect and have advanced a new qualitative method for predicting the presence or absence of specific microwave effect in organic reactions. The results can be summarized in the form of following rules:

Reactants			Specific microwave effect
A	+	B ⟶	Products
Polar		Polar	Observed/ allowed
Polar		Non-polar	Not observed/dis-allowed
Non polar		Non polar	Dis-allowed

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