Naphthalene Substitution

S. V. SUNTHANKAR*

THE substitution reactions of naphthalene are much more complex than those of benzene. Unlike benzene, naphthalene possessing a bicyclic aromatic structure, can give two mono-substitution products and the possible disubstitution isomers are ten or more (if the substituents are different) as against only three in the benzene series. Further, the reaction temperature has a considerable effect on the orientation of substituents. Particularly, in the sulphonation of naphthalene and its derivatives, the orientation is profoundly temperature dependent. For example, at a lower temperature (40°), α-naphthalenesulphonic acid is the major product (96% yield) and at a higher temperature (160°), the β-isomer is obtained in 85% yield[1,2]. This interesting fact has been conveniently exploited by dyestuff technologists for the commercial preparation of the desired naphthalenesulphonic acids.

The reactions of naphthalene, in general, can be explained according to the "electronic theory" which has been used very successfully to explain benzene substitutions[3]. However, because of the wider possibilities and the pronounced temperature dependence of some of the reactions, it seems that other factors, which have been overlooked for simplification in benzene substitution, will have to be taken into account for a clearer understanding of naphthalene substitution. It is no wonder, therefore, that the rigorous application of the resonance theory to naphthalene substitution has led its champions into an embarrassing situation[2,4].

In order to understand the nature of a chemical reaction, it is necessary to consider the various factors governing its rate. Two theoretical approaches have been forwarded to interpret reaction kinetics[3,5,6]. The first one is the collision theory and the second is the transition state theory. To maintain brevity, only the essential points of the two will be touched here; lest the clarity of the discussion will be affected by mathematical derivations.

A reasonable hypothesis of the collision theory is that molecules must collide in order to react. This implies that the rate of a reaction should be dependent on the frequency of collision. Actual calculations of the rates of bimolecular reactions, however, have shown that the rates so calculated according to the kinetic theory are much smaller. This discrepancy has been explained by supposing that collisions will be effective if the reacting molecules are properly orientated and possess a certain amount of energy, known as activation energy. The first condition necessarily brings in an idea of steric factor which governs the probability of collision. A rate equation, modified to meet the above conditions, is given by

$$k = PZ_0\, e^{-E/RT} \quad \ldots\ldots\ldots\ldots (1)$$

where k is the velocity constant, P the steric or probability factor, Zo the collision frequency at unit reactant concentration, E the activation energy, R the gas constant, T the absolute temperature and e the base of the natural system of logarithms.

According to the other theory, a reacting system is supposed to pass through a transition state—a state of much more than usual amount of energy; and therefore no sooner such a complex is formed it collapses in either way, without a

---

*Reader in Colour Chemistry, B.U.D.C.T.

further supply of energy, to give the products or the reactants[3,5]. The rate of a reaction, therefore, is governed by the equilibrium between the reactants and the transition state. Since an equilibrium is dependent on the differences in entropy and heat-content between the reactants and the products, the rate of a reaction can be related to the differences in the energy and entropy of the reactants and the transition state. These differences are called the energy of activation and the entropy of activation respectively. By taking into account the normal thermodynamic properties of the transition complex, *the velocity constant* (*k*) *of the* reaction can be equated as

$$k = S\, e^{-E/RT} \text{ .... } (2)$$

$$k = \text{a constant } \times T\, e^{\Delta S/R} e^{-E/RT}$$

where S is the entropy factor, ΔS is the entropy of activation and E is the activation energy. Thus, the equations I and 2 are indentical (if $PZo = S$). However, their growths are different; one is developed on the kinetic theory and the other on the thermodynamic probability. Now, the entropy of a molecule is a function of the kinetic energy associatea with the modes of vibration and rotation, and cannot be determined in any simple way by the bonds in it; although it has been possible to calculate the entropies of a few simple molecules and a few simple transition complexes. Therefore, a convenient assumption is made that the differences in the entropy of activation play a negligible part in determining reaction rates; which means that the rate of a reaction depends on the activation energy only. This assumption has been satisfactorily verified in the substitution of benzene derivatives with the notable exceptions of ortho-substitutions, in which the entropy of activation is much lower. This ortho effect is classified under a general term of steric hindrance, which obviously lowers the entropy of activation by reducing the effective degrees of freedom of the transition complex.

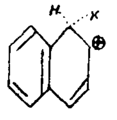
The neglect of the entropy of activation leaves us with the other alternative of predicting reaction rates by the activation energy, which is the energy required to take the reactants to the transition complex. Since the transition complex breaks into the products without any further supply of energy, the rate of a reaction will be higher, the lesser is the activation energy. Just as the entropy of activation is related to the difference in the kinetic energy of the reaction system, the activation energy can be supposed to be related to the potential energy differences, which are primarily dependent on electronic displacements. The activation energy, therefore, is governed by the bond-energy and the resonance-energy differences. The bond-energy differences arise because of the fact that during a reaction, the bond-breaking and the bond-forming is only partial (which is suggestively denoted by dotted lines in the transition state) and hence the bond energies of the reactants and that of the transition complex will differ. Similarly, the reasonance-energy differences arise out of the fact that both the reactants and the transition state have certain resonance-energy. If a reaction involves an increase in resonance-energy, the transition state will have higher resonance-energy and the reaction will be faster. Similarly, if the reactants can give two transition states to lead to two different products, the one which is resonance-energy rich will be favoured.

In aromatic substitutions, the bond-energy differences can be neglected and the orientation can be discussed primarily on the resonance-energy effects. This means that in such reactions, the activation energy is dependent on the reasonance-energy differences only.

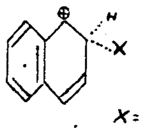
With these theoretical considerations, let us now try to rationalise some of the substitution reactions of naphthalene, giving due attention to different factors which can be operative in such reactions.

The sulphonation will be a preferred illustration to start with, because this reaction is so-called abnormal being profoundly temperature-sensitive ; and secondly there is considerable information in the literature on this reaction, since the naphthalenesulphonic acids are used for the preparation of valuable dye-intermediates.

In the sulphonation of aromatic compounds, the reactive species can be supposed to be the $\overset{+}{SO_3H}$ cation, which being positively charged is electrophilic, and will try to attack the carbon at which the electron density can be more. Unlike in benzene, there are two positions, the α- and β-, in naphthalene ; and an electrophilic attack at these sites will give rise to two transition states[6] formulated as



I



II

X = SO_3H

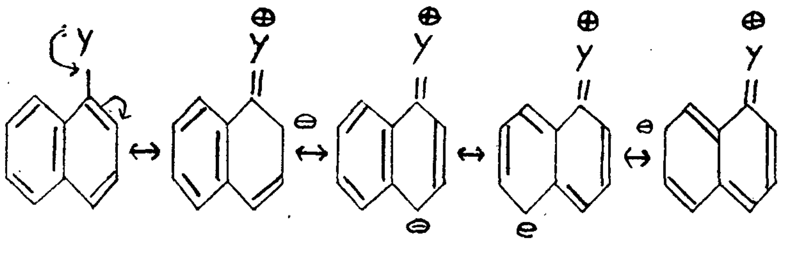
Now, the α- attack creates a phenylallyl ($C_6H_5-CH=CH—\overset{+}{C}H_2\ldots$) type cation and the β- attack creates a benzyl ($C_6H_5-\overset{+}{C}H_2\ldots$) type cation in the transition states. The former will be more stable because of the extended conjugation resulting in more resonance energy. In fact, the quantum mechanical calculations have shown that the resonance energy of phenylallyl cation is 61 cals, and of benzyl cation 52 cals. which implies that the activation energy of the α- substitution is less than that of the β-. The α- site, however, is flanked by the peri C-H, and therefore the entropy of activation for the α- substitution should be less. In other words, the activation energy favours the α- site and the entropy of activation the β- site. Since at lower temperatures, the α- acid predominates, it seems that the activation energy plays a dominating part and at elevated temperatures, the entropy factor seems to determine the course of the reaction. The velocity constants of the two reactions can be given by

$$k\alpha = S\alpha\, e^{-E\alpha/RT}\,;\quad k\beta = S\beta\, e^{-E\beta/RT}$$

where $S\beta > S\alpha$ and $E\beta > E\alpha$

At a lower temperature the energy factor $e^{-E\alpha/RT}$ is much greater than $e^{-E\beta/RT}$ and therefore $k\alpha > k\beta$ and the α- substitution predominates, but at a higher temperature when the ratio of exponential terms become smaller, the entropy term (or PZ factor) seems to be the rate-determining factor, resulting into the β-product (i.e. $k\beta > k\alpha$).

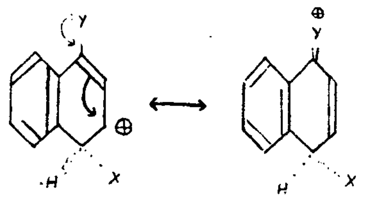
Further substitution of naphthalene, although complex, can be explained on similar grounds. In the electrophilic substitutions, now under consideration, one of the rings of naphthalene, in the transition state, becomes positively charged and the other almost retain its benzenoid structure. In the transition state, naphthalene gives rise to the benzyl and the phenylallyl type cations, by which the charge is concentrated in the charged ring. A substituent, therefore, will have a greater effect on the



III IV V VI

charge if it is in the charged ring. The effect of a substituent on the charge will be clear by taking a specific example of an electron-releasing substituent. The above resonance structures can be written for such a derivative.

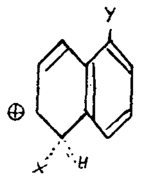
The α-Y-substituent due to its electron-releasing tendency activates the 2-, 4-, 5- and 7- positions for electrophilic substitutions. This means that if substitution takes place at any of these places, say for example at the 4- position, the positive charge created at the 3- carbon atom is partially stabilized by the electron-releasing tendency of the Y-group, as formulated below.



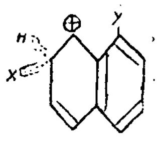
VII VIII

Such a kind of charge stabilization is not possible if the substitution takes place at the 3- position.

An electron-releasing group at the α-position activates the 5- and 7- positions weakly, because these activations are effected at the cost of the benzenoid resonance of both of the rings (as in V and VI). The substitution, if it occurs in the other ring will, therefore, take place preferentially at the 5- position, because such an attack will produce a transition state involving a phenylallyl type cation (IX) than a benzyl cation (X) which is created by an attack at the 7- position.

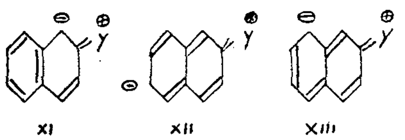


IX



X

Similarly, the activating effect of an electron-releasing substituent at the β-position can be given by the following resonance structures.



XI XII XIII

For the same reason, in such naphthalene derivatives the adjacent α- position is activated strongly and the 6- and 8- positions weakly.

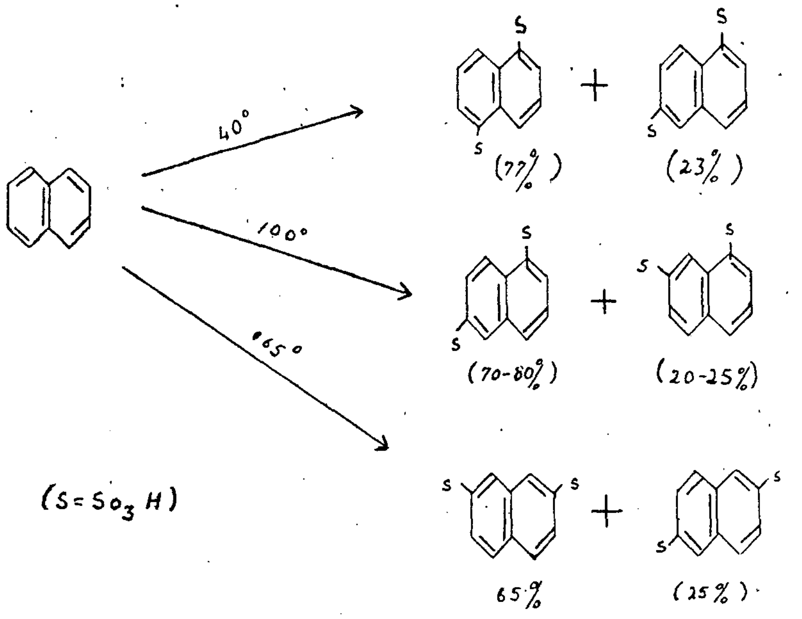
Conversely, the deactivating effect of an electron-withdrawing group will be more in its own ring and such a group generally orients further substitution in the other (unsubstituted) ring. Because of its resonance effect, a negative α- substituent will deactivate the 5- and 7- positions more strongly than the 6- and 8- positions, and a β- substituent will have an opposite effect on the other ring. The corresponding canonical structures for a negatively substituted naphthalene are as above (III to VI and XI to XIII) with the charges reversed.

For a discussion of di-substitutions, we shall start again with the sulphonation of naphthalene. 1-Naphthalenesulphonic acid on further sulphonation at 57°, gives 75% of 1,5, 10% of 1,6 and 15% of 1,3 and 1,7—disulphonic acids[7]. Similar results are obtained by direct slulphonation of naphththalene (see chart 1).

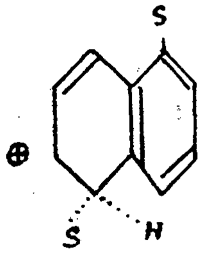
Below 40°, naphthalene gives mainly the 1,5-disulphonic acid (77%) and the 1,6-acid in 23% yield. As the temperature of the rection is raised to about 100°, the 1,6- acid is the major product together with some 1,7- acid (20-25%). At a still elevated temperature (165°), the 2.7- acid (65%) and the 2,6- acid (25%) are formed[1].

CHART I

Disulphonation of Naphthalene



According to the above considerations, the sulphonic group (SO_3H), being an electron-withdrawing group, should deactivate the 5- and 7- positions. However, at lower temperatures 1,5-acid is the major product. This suggests that the activation energy due to the transition state involving a phenylallyl cation, (XIV) outweighs other factors. However, as the temperature of the rection is raised, both the entropy effect and the deactivating effect of the substituent seem to become more operative. The former gives an alternative between the 6- and 7- positions but the latter gives a decision in favour of the 6- position only; and in fact, at 100° the 1,6- acid is obtained in 80% yield.



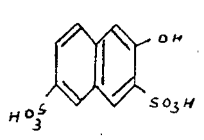
XIV

Similarly, naphthalene-β-sulphonic acid gives the 2,5- acid in cold and the 2,6- and 2,7- acids at elevated temperatures[1]. Of the β-substituted acids, the yield of the 2,7- acid is more (65%) than that of the other isomeric 2,6- acid (25%), because the deactivating effect of the β-SO_3H group on the 6- position makes the 7- position more favourable for an attack.

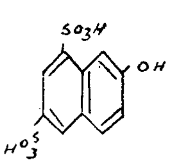
Further sulphonation of naphthalene gives the expected products, the SO_3H group entering the *m*-position to the acid substituent already present in the ring. This, however, suggests that when each of the naphthalene rings is deactivated by the SO_3H substituent, the *meta* orienting effect of the SO_3H group predominates over other factors. The other important observation that two sulphonic acid groups never enter the *peri* or the ortho positions to each other is obvious on steric grounds.

The sulphonation of napthalene derivatives can be explained on similar lines, although some of the information in the literature is to be rechecked on the above theoretical predictions. For example, the sulphonation of α naphthol, at about 50° gives 1-naphthol-4-sulphonic acid (NW-acid) and 1-naphthol-2-sulfonic acid (20%), and at elevated temperatures (125-130°) the 2,7-disulphonic acid is formed. Since the ring containing functional group is activated, the first choice for the attacking $\overset{+}{S}O_3H$ is the 2- and 4-positions; and at the elevated temperature, the substitution is at the β- positions (2 and 7), which are activated by the α-OH group. Further sulphonation of α-naphthol, as predicted, gives 1-naphthol-2,4,7- trisulphonic acid.

Similarly, sulphonation of β- naphthol (35°) gives mainly the 1-sulphonic acid (70%), and at 50-100°, the products are the 6- and 8- sulphonic acids. The proportion of the 6- acid (Schæffer acid) increases as the reaction temperature is raised. A prolonged action of sulphuric acid at 110°, gives *R*- and *G*- acids. In this case also, the yield of *G*- acid is higher at lower temperatures and that of *R*- acid at elevated temperatures. These results are obvious, except the formation of *R*- acid which involves the 3-position. According to the resonance effect of the β- hydroxyl group, the 3- position is not supposed to be particularly activated for electrophilic substitutions[8], and therefore the attack of $\overset{+}{S}O_3H$ cation at this position emphasizes the importance of the entropy factor on the course of the raction at higher temperatures.

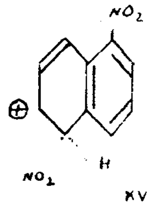


R-ACID

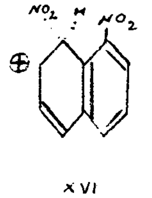


G-ACID

Let us now turn to another reaction i.e. the nitration of naphthalene. This particular reaction proceeds very readily and the mono-substitution product almost exclusively is α-nitronaphthalene. Unlike sulphonation, the nitration of naphthalene cannot be carried out at higher temperatures and the β-isomer can be realized up to 5%, under special conditions only. It seems that the activation energy is the controlling factor in nitration and favours the α-orientation for the reason stated above. The nitro-substituent, being a deactivating one, orients further nitration in the unsubstituted ring. For an electrophilic substitution, the 1-nitro group deactivates the 5- and 7- positions because of its resonance effect, leaving a choice between the 6- and 8- positions for the entering $\overset{+}{N}O_2$ cation. The dinitration products, however, are the 1,5- and 1,8-isomers. The dinitration, therefore, seems to be influenced by the energy-rich phenylallyl type cations created in the transition states, such as



XV



XVI

Now, there are some factors favourable as well as unfavourable for each of the 5- and 8- substitutions. For the 5-substitution, the resonance energy of the transition state is favourable, but the deactivating effect of the 1-NO_2 group and to some extent the steric hindrance of the *peri* CH are unfavourable. Whereas, for the 8-substitution, both the reasoance-energy of the transition state and the absence of the direct deactivating effect of the 1-nitro substituent are favourable, the added steric hidrance becouse of the bulky nitro group attached to the *peri* carbon atom is unfavourable. In fact, in the dinitration mixture the yield of 1,8-dinitronaphthalene is twice that of its 1,5-isomer. This emphasizes that the entropy effect or the steric factors play a negligible rôle in the nitration of naphthalene. Interestingly, further nitration of 2-nitronaphthalene gives[9] a mixture of 2,5- and 2,8- dinitrocompound and 1,3,8-trinitro derivative in a ratio of 42:50:10, (± 5%) respectively. In this case also the nitro substituent prefers the α-positions (5 and 8-) although the deactivating effect of the nitro group is at the 8-position.

Thus, the substitution reactions of naphthalene, which are generally supposed to be too complex to explain, can be qualitatively rationalized to a large extent by giving due consideration to various factors which can be operative, depending upon the conditions of the reactions and the nature of the substituents.

REFERENCES :

1. Venkataraman, " The Chemistry of Synthetic Dyes ", Vol. 1, Academic Press, New York, 1952, p. 76-197.
2. Lubs, " The Chemistry of Synthetic Dyes and Pigments ", Reinhold Publ. Crop., New York, 1955, p. 65-95.
3. Remick, " Electronic Interpretations of Organic Chemistry ", 2nd ed. John Wiley and Sons, Inc., New York, 1949, p. 58-229.
4. Vasely and Jakes, **Bull.Soc.Chem.**, 1923, **33**, 952.
   Hodgson and Hathaway, **J.Soc.Dyers Colourists,** 1945, **63**, 109.
   Hodgson and Ward, **ibid.**, 1947, **63**, 141, 177 etc.
5. Hammett, " Physical Organic Chemistry ", McGraw-Hill, New York, 1940, p. 69-130.
6. Dewar, " The Electronic Theory of Organic Chemistry ", Clarendon Press, 1949, p. 21-30 ; 160-177.
7. Spryskov and Karavaev, **J.Gen.Chem. U.S.S.R.**, 1953, **23**, 1712.
8. Wheiland, " The Theory of Resonance and its application to Organic Chemistry ", 2nd ed., John Wiley and Sons, Inc., New York, 1945, p. 269.
9. Ward and Hawkins, **J.Chem.Soc.**, 1954, 2975.