

THE ACID-CATALYZED REARRANGEMENT AND DISPROPORTIONATION OF AROMATIC
HYDRAZO COMPOUNDS. COMMENTS ON THE PAPER BY V. O. LUKASHEVICH.

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In a recent paper (1) Lukashevich has summarized his views on the rearrangement and disproportionation of aromatic hydrazo compounds. These views deny the validity of current interpretations of the mechanism of the acid-catalyzed benzidine rearrangement, interpretations which have been based on extensive kinetic studies by several groups. Lukashevich's views on acid-catalyzed disproportionation are also in conflict with kinetic evidence, and, like those on rearrangement are in error. These views are discussed and contrasted with experimental facts in the following pages.

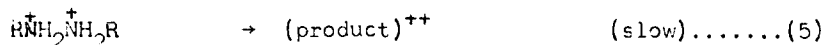
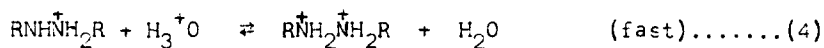
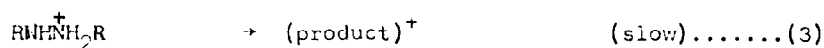
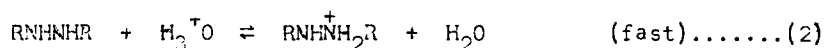
Rearrangement.

The current, generally-accepted interpretation of acid-catalysis in the benzidine rearrangement is expressed in equation 1 (2,3). This equation says

$$-d(\text{Hyd})/dt = k_2[\text{Hyd}][\text{H}^+] + k_3 [\text{Hyd}][\text{H}^+]^2 \dots\dots\dots(1)$$

that the disappearance of the hydrazo compound (Hyd) is first-order in hydrazo compound, and may be both first- and second-order in acid. The facts of the equation have been well documented. Some hydrazo compounds have been shown to rearrange solely by first-order acid catalysis (4); in those cases the importance of the second term in equation 1 was negligible. Some hydrazo compounds have been shown to rearrange solely by second-order catalysis (4-9); in those cases the importance of the first term in equation 1 was negligible. Last, some hydrazo compounds have been shown to rearrange by both first- and second-order acid catalysis, and with some of these compounds the transition

from first- to second-order has been clearly shown as taking place with increasing acidity (4,10). The details of the steps that are summarized by equation 1 have been elucidated by studies of kinetic- and solvent-isotope effects (4,11). The steps are the fast, reversible protonations (equations 2 and 4) and the slow rearrangement of the mono- and di-protonated molecules (equations 3 and 5). That is, acid-catalysis has been shown to be specific acid-catalysis for both the one- and the two-proton processes. (Whether or not intermediates are involved in the steps 3 and 5 is not relevant to the present discussion. The question is discussed in reference 13.)



Lukashevich's view (1) is that the acid-catalyzed rearrangements do not occur as described by equations 2-5. Lukashevich's view is based primarily on the results of his work with the salts of aromatic hydrazo compounds, published in more detail in earlier papers, one of which, as a matter of fact, is entitled: "evidence refuting double protonation of hydrazo compounds during rearrangement" (12). The essence of Lukashevich's view is apparently based on the failure to obtain di-acid salts by treating hydrazo compounds with hydrogen chloride or hydrogen bromide in non-polar solvents such as ether or a mixture of benzene and toluene. Some hydrazo compounds formed an isolable salt, but the salt was always the mono-acid salt. A mono-protonated hydrazo molecule is regarded as being too weakly basic to accept another proton, so that the theory which incorporates the steps shown in equations 4 and 5 is regarded as wrong. The fallacy in this argument must be evident. It is not uncommon in chemical reactions that an intermediate is detectable (kinetically or otherwise) but not isolable. The kinetic evidence for the di-protonation is so strong that it cannot be refuted by the failure to isolate a di-acid salt.

It is Lukashevich's view, furthermore, that although a mono-acid salt is formed by a hydrazo compound, the salt will rearrange only under continued action of an acid. Thus, the mono-protonated hydrazo molecule is regarded as being incapable of spontaneous rearrangement. Lukashevich represents the transition state for all rearrangements as in expression 6. The error in these

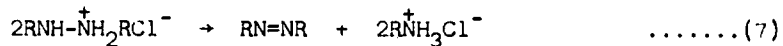


conclusions must surely be evident. Suppose we accept Lukashevich's view that di-protonation cannot occur. Mono-protonation must surely not be a rate-determining process. The transfer of a proton between nitrogen and oxygen atoms (in aqueous-organic solvents for which the only reliable kinetic data are available) is fast. In that case, the transition state shown in expression 6 is for a reaction which is first-order in hydrazo compound and second-order in acid. If we accept the addition of the first proton to be fast and reversible (that is, as in equation 2), and also accept Lukashevich's view that rearrangement can occur only with the mono-protonated molecule and "only when the acid exerts continued action" (1), all of the rearrangements which take place in ionizing solvents should be second-order in acid. This situation cannot be accommodated with the now well-documented kinetics. If, on the other hand, we accept only Lukashevich's view about non-spontaneous rearrangement and the continued action of acid, the way of achieving first-order acid catalysis must be to have the reverse step of equation 2 (the de-protonation) much slower than the reaction of the mono-protonated ion with the second proton. It is not clear from the article (1) if this kinetic description is what Lukashevich intends, but, in any case it cannot be accommodated with well-documented kinetics either.

The transition state represented by expression 6 represents (as far as can be surmized in the absence of a more detailed description) the rate-determining involvement of an acid (the hydronium ion) and substrate. The reaction described by this transition state should be general acid-catalyzed. It is not possible to accommodate the known solvent-isotope effects (4) with this description.

Disproportionation

This reaction is represented by Lukashevich as occurring between two mono-protonated hydrazo molecules (equation 7). Suppose, again, that this is



correct. The rate of mono-protonation of an uncharged hydrazo compound must surely be greater than the rate of the bi-molecular reaction of equation 7. In that case and if equation 7 is correct the disproportionation reaction must be second-order in hydrazo compound. This requirement contradicts every known case in which the kinetics of hydrazo disappearance has been measured. It is well established that rearrangement is first-order in hydrazo compound. Some hydrazo compounds (particularly the 4,4'-disubstituted, to which Lukashevich addresses himself) undergo concurrent rearrangement and disproportionation. Where the rate of disappearance of these hydrazo compounds has been measured, no other than first-order hydrazo dependence has been found. In connection with concurrent rearrangement and disproportionation Lukashevich states that "an attempt to determine the kinetic order of two parallel reactions is without justification." This clearly contradicts the work of Carlin and Wich with p-hydrazotoluene (7). These workers showed that p-hydrazotoluene is converted into an o-semidine, p-toluidine and p-azotoluene. The overall disappearance of p-hydrazotoluene was first-order in p-hydrazotoluene. However, it was shown directly and separately that the fractions of the p-hydrazotoluene being converted into the o-semidine and p-toluidine did not vary during the course of a run. It was concluded (justifiably) that the fraction being converted into p-azotoluene did not vary with time. Thus, where the three products were formed concurrently in relative concentrations invariant with time, the conclusion that their formation followed one kinetic law (i.e., first-order in p-hydrazotoluene) is valid. More recently, it has been shown that p-hydrazobiphenyl undergoes concurrent rearrangement and disproportionation, the disproportionation accounting for 75-88% of the hydrazo compound (13). The disappearance of the hydrazo compound was clearly first-order in

hydrazo compound and second-order in acid (above an acidity of 0.0306 M). Here there should be little need to determine the kinetics of the disproportionation reaction separately.

In summary, Lukashevich's views on the acid-catalyzed rearrangement and disproportionation are inconsistent with reliable kinetic data reported by a variety of research groups. The mechanisms proposed by Lukashevich would entail kinetic characteristics completely contradictory of those which are well established.

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