JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 2, 491–506 (1989)

REVIEW COMMENTARY

REFLECTIONS ON THE π-COMPLEX THEORY OF BENZIDINE REARRANGEMENTS*

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ABSTRACT

The ups and downs, and reasons therein, of the π-complex theory of the mechanism of the benzidine rearrangements, and the possible role of π-complexes in a newer understanding of the rearrangements, are described.

This paper concerns the mechanism of the benzidine rearrangement, the thought-provoking role that Dewar had in it during the 20-year period 1945–65 and the current view. The paper is designed first to try to understand why Dewar's then innovative π-complex theory met so much opposition and rejection, second to try to set the record straight as to who was right or wrong about benzidine rearrangement mechanisms in the early days and last to record where knowledge of the rearrangement stands now. Twenty years or so have elapsed since the end of the heady period of the 1950s and 1960s when battles over the mechanism of the benzidine rearrangement took place in the journal literature, principally between Dewar on the one hand and Banthorpe, Ingold and Hughes on the other. Joining the battles were others, including myself and coworkers bent on testing Dewar's ideas, and more often than not criticizing them. The big guns have ceased to fire, the smoke has (hopefully) cleared and the opportunity seems to be at hand to look at what was going on.

The benzidine rearrangements are best known as the acid-catalyzed, intramolecular rearrangements of hydrazoarenes. Thermal benzidine rearrangements are known, to which I shall also refer, and even photochemical ones,[1] but the focus of attention for so many years was on the acid-catalyzed rearrangements. These are illustrated for reference in equations (1)–(4). Equation (1) shows that hydrazobenzene (**1**) itself rearranges into benzidine (**2**), from which the class name is derived, and diphenyline (**3**). Under conditions in which most kinetic and mechanistic studies have been carried out, the ratio of the yields of **2** and **3** is approximately 70:30. Equations (2) and (3) are for guidance only, rather than as explicit descriptions of

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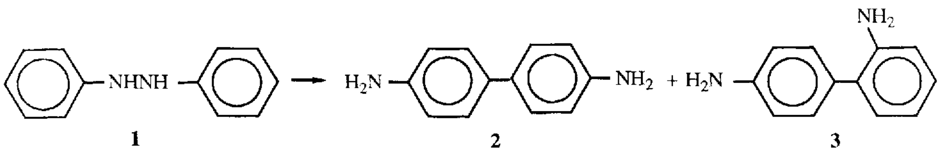
* Dedicated, with respect, for the 70th birthday of Professor Michael Dewar, who, on scribbled, lunch-time table napkins at the 1961 American Chemical Society meeting in Chicago tried but (fortunately) failed to convince me of the validity of his π-complex theory. I wish I had kept the napkins.

0894–3230/89/070491–16$08.00

Received 28 September 1988
Revised 21 November 1988



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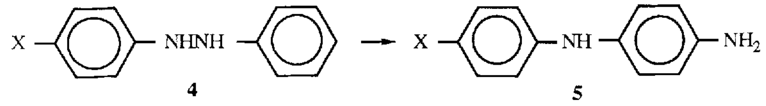

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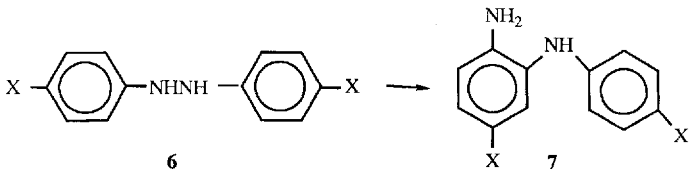

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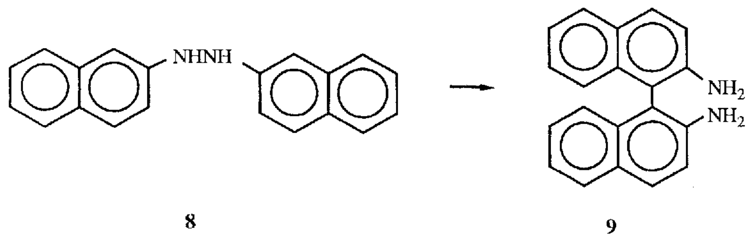

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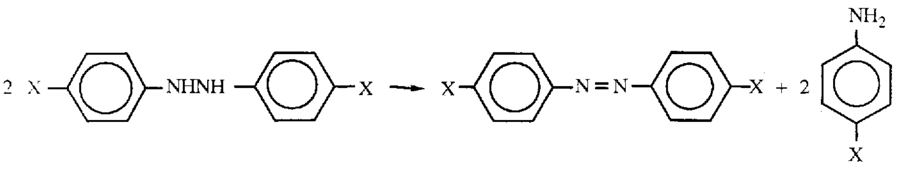


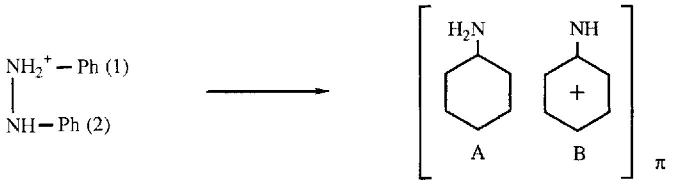
(5)

particular cases. That is, a 4-substituted hydrazobenzene [**4**, equation (2)] can give a *p*-semidine (**5**), while a 4,4′-disubstituted hydrazobenzene [**6**, equation (3)] can give an *o*-semidine (**7**). In practice, mixtures of diphenyline, *o*- and *p*-semidine types may be obtained from particular *p*-substituted hydrazobenzenes. *o*-Benzidine rearrangements are also known, but are best seen in the rearrangements of hydrazonaphthalenes, for example, as in equation (4). Accompanying all benzidine rearrangements, either to a very small or to a very large extent depending on the arene structure, is a disproportionation reaction, shown with a 4,4′-disubstituted hydrazobenzene in equation (5).

Explicit mechanistic information about the benzidine rearrangements was scant when interest in their mechanisms began to develop in the years 1930–40. A large compilation of products of all of the then known rearrangements had been assembled by Jacobson in 1922,[2] but the data in this compilation suffered from the relative imprecision of experimental work of the times, and from the variety of ways in which rearrangements had been carried out. Often, for example, a hydrazoarene was prepared and rearranged *in situ* by heating the corresponding azoarene with tin and hydrochloric acid, a practice which led inevitably to excessive disproportionation and also some reductive scission.

In this early period Robinson[3] and Hughes and Ingold[4] proposed mechanisms of rearrangement designed, among other things, to account for intramolecularity.[5] The mechanisms called for electron flowings, which in modern terminology could be equated with a concerted process. Robinson depicted rearrangement as beginning with the *N*-monoprotonated hydrazoarene.[3] Hughes and Ingold, on the other hand, curiously, were insistent that protonation did not precede N—N heterolysis. A nearby proton was called upon to 'disturb the electronic system of the benzidine molecule' (presumably they meant the hydrazobenzene molecule) and to be present in the transition state, yet not to protonate the hydrazoarene. Perhaps they meant by this that the approach of a proton was to be coincident with the breaking of the N—N bond. It seems clear that they intended rearrangement to be a continuous process.

A radically different and novel proposal was made by Dewar for the first time in 1945.[6] Dewar proposed that a non-localized π-electron migrated from ring 2 to ring 1 of the monoprotonated hydrazobenzene [equation (6)], with consequent fission of the N—N bond. Thereby a complex molecule was formed 'composed of the aniline derivative (A) and the ion radical (B),'[6] and this was called a π-complex. Provision was made for collapse of this complex to a benzidine-type product or, by rotation of the two halves of the complex before collapse, for the formation of other types of rearrangement product.



(6)

It is extraordinary to reflect now that at that time all proposals for the mechanism of rearrangement assumed that the monoprotonated hydrazoarene rearranged. No one in that period of interest had taken the trouble to measure the kinetic order in acidity, and all had overlooked that van Loon had done that almost 40 years earlier in his thesis work in Gröningen.[7,8] Another attempt to relate rates of rearrangement to acidity had been reported, in fact, by Biilmann and Blom in 1924, in a study of redox characteristics of pairs of azo- and hydrazoarenes.[12] Biilmann and Blom found that the rate of rearrangement did increase with increasing hydrogen ion concentration, but because of the complexity of their approach they were unable to find the proportionality. It is interesting that this report, too, did not spur others on to trying to find the kinetic order in acid. It was the kinetic order in acid, in fact, that was to bring about the first rejection of Dewar's ingenious idea, and lead it later into further trouble.

In 1946 Dewar measured the rate of rearrangement of hydrazobenzene, *o*- and *m*-hydrazoanisole and *p*-hydrazotoluene in aqueous ethanol.[13] The relative rates were taken as supporting the π-complex mechanism. However, the kinetic order in acid was not measured, being assumed instead to be unity in each case. This was the position also, slightly later, when Dewar elaborated, in his book,[14] on the role of the π-complex in the benzidine rearrangements, showing how it could account for the effect of substituents on the type of rearrangement and on relative rates.

In 1949, G. S. Hammond and I, having no interest in the benzidine rearrangement other than a casual curiosity about its mechanism, noticed Dewar's oversight in kinetic acidity.[13] We decided, therefore, to measure the kinetic order of acid in the rearrangement of hydrazobenzene and, to our surprise, found it to be 2·0.[15]

The finding of second-order acid kinetics[11,15] was, of course, no support for Dewar's mechanistic ideas. It also initiated a renewed interest in the benzidine rearrangement in a number of places, but particularly in Ingold's laboratory in England. Soon it was to be shown by Carlin and by Ingold that some benzidine rearrangements were first order and others second order in acid, while some could show both dependences, depending on the acid concentration. The story on this and other developments has been set out in much detail by Banthorpe, Hughes and Ingold[18] and has been summarized in a number of reviews.[19–22]

The finding of variable kinetic order in acid placed the π-complex theory under a cloud which obscured any intrinsic merit the theory might have had. Among the compounds whose rates of rearrangement Dewar had measured and compared under the assumption of first-order acid kinetics were hydrazobenzene and *p*-hydrazotoluene, both of which were found to rearrange under second-order acid catalysis. It is not surprising, therefore, that the π-complex theory was given short shrift.

$$\mathrm{ArNHNHAr} + \mathrm{H}^+ \rightleftharpoons \mathrm{Ar}\overset{+}{\mathrm{N}}\mathrm{H_2NHAr}$$

$$\mathrm{Ar}\overset{+}{\mathrm{N}}\mathrm{H_2NHAr} \rightleftharpoons \pi\text{-complex}$$

$$\pi\text{-complex} + \mathrm{H}^+ \rightarrow \text{product}$$

Scheme 1

The problem for the π-complex theory over kinetic order in acid was compounded later when Dewar fitted to his theory a provision for variable order in acid. The provision was that the first protonation of a hydrazoarene led to the reversible formation of a π-complex. The function of the second proton was to attack the π-complex and carry it on to rearrangement products (Scheme 1).[23–25] Again, provision was made for rotations within the π-complex so that appropriate conformations could be reached before the second product-forming reaction took place. At that stage of the π-complex theory, a key characteristic applied to the π-complex was that it should retain its asymmetry right up to the product-determining step, and Dewar felt that if a diprotonated hydrazoarene rearranged the products would be difficult to explain.[24] A number of predictions and/or explanations were made on the basis of this revised formulation of the π-complex theory[24,25] which were shown later to be contrary to fact, and the π-complex theory suffered accordingly. Thus, Dewar's kinetic derivations predicted that if a hydrazoarene could rearrange by both first- and second-order acid kinetics, it would rearrange by second order at the lower and by first order at the higher acidity. Later, it was shown that the opposite behavior held.[18] Dewar predicted that bulky substituents placed in the *para* positions of hydrazobenzene should reduce the kinetic order in acid; the more the bulkiness, the greater the trend toward first order.[24] In time it was shown that the second-order acid kinetics of hydrazobenzene[11,15] and *p*-hydrazotoluene[17,26] were also in control in the case of 4,4′-di-*tert*-butylhydrazobenzene,[27] with the result that the π-complex theory was again discredited. Further damage to the π-complex theory occurred when Dewar accepted an old literature report that 4,4′-diphenylhydrazobenzene disproportionated entirely rather than rearranged,[28] and attributed this behavior to the inability of the two biphenyl moities to line up in the initially required π-complex.[23-25] Later, Shine and Stanley showed that if reaction was carried out in aqueous ethanol at 0 °C rather than by heating with concentrated hydrochloric acid, rearrangement did occur, to the extent of 25%, and with second-order acid kinetics.[29]

The problems with the π-complex theory described above and which gave fuel for scepticism and criticism of its validity were removed in 1965 with a reformulation by Dewar and Marchand.[30] This formulation (Scheme 2) embraced not only first- and second-order acid catalysis but also the thermal, neutral rearrangement of hydrazoarenes which were uncovered in my own laboratory[31] and elaborated on in Ingold's.[18] A very simple adjustment was made for the rate-determining formation of a π-complex in each rearrangement from a neutral, monoprotonated and diprotonated hydrazoarene. The new equations (Scheme 2) could account easily for the kinetics of acid-catalyzed rearrangements, and, in Dewar's view, for the effect of substituents on rates and product types.

$$
\begin{aligned}
\mathrm{ArNHNHAr} &\rightarrow \pi_0 \qquad \text{(slow)}\\
\pi_0 &\rightarrow \text{products}\\
\mathrm{ArNHNHAr} + \mathrm{H}^+ &\rightleftharpoons \mathrm{Ar\overset{+}{N}H_2NHAr}\\
\mathrm{Ar\overset{+}{N}H_2NHAr} &\rightarrow \pi_1 \qquad \text{(slow)}\\
\pi_1 &\rightarrow \text{products}\\
\mathrm{Ar\overset{+}{N}H_2NHAr} + \mathrm{H}^+ &\rightleftharpoons \mathrm{Ar\overset{+}{N}H_2\overset{+}{N}H_2Ar}\\
\mathrm{Ar\overset{+}{N}H_2\overset{+}{N}H_2Ar} &\rightarrow \pi_2 \qquad \text{(slow)}\\
\pi_2 &\rightarrow \text{products}
\end{aligned}
$$

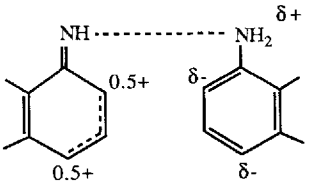
Scheme 2

During the 1960s a large amount of kinetic and product data were being gathered, especially in Ingold's laboratory. This large body of information was fitted by Banthorpe, Hughes and Ingold to a theory of rearrangement called the polar transition state (PTS) theory. The idea behind this theory was the after equilibrium mono- or diprotonation at the nitrogen atoms, the N—N bond of the hydrazoarene began to break heterolytically. In that way a polar transition state developed, in which one half of the breaking protonated molecule became positively charged while the other half remained neutral. While the N—N bond stretched the molecule adopted a conformation in which bonding for product formation began. Representations[18] of the polar transition states for a one-proton (1,1′-hydrazonaphthalene) and a two-proton (hydrazobenzene) rearrangement are shown here as PTS^+ and PTS^{2+}. Banthorpe, Hughes and Ingold used this concept to explain their views of the kinetic data and formation of the products of all benzidine rearrangements, except for *p*-semidines, whose formation at that time was still thought to require the presence of heavy-metal ions.[18] Another theory, calling for caged radical and cation radical pairs, was also in vogue, but did not have a solid basis of support.[18-22]

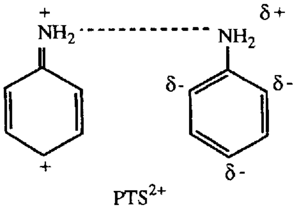
Later, a fourth theory, the so-called ring-protonation theory, commanded some interest,[32] but was never supported by acceptable experimental data, and was finally discredited.[33-35]

Principally, therefore, two powerful theories of the benzidine rearrangements held sway during and following the mid-1960s: the π-complex and the PTS theories. The π-complex theory survived its earlier criticisms in its final formulation, while the PTS theory was promoted vigorously by Banthorpe, Hughes and Ingold. Neither side of adherents was bashful about criticizing the other.

Now, Dewar and Marchand pointed out the crux of the matter, that the kinetic evidence could not distinguish between these mechanisms.[30] In fact, a stand-off resulted, and whether one believed in the π-complex or the PTS theory became a matter of personal intuition or prejudice.



PTS$^+$

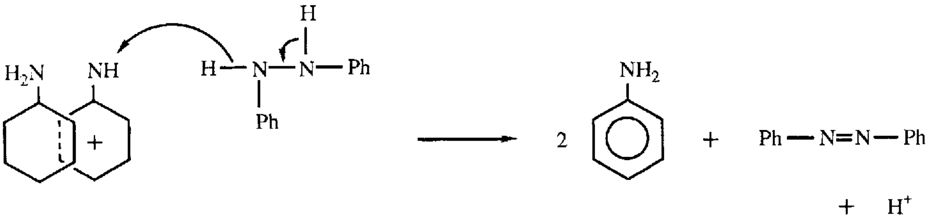


PTS^{2+}

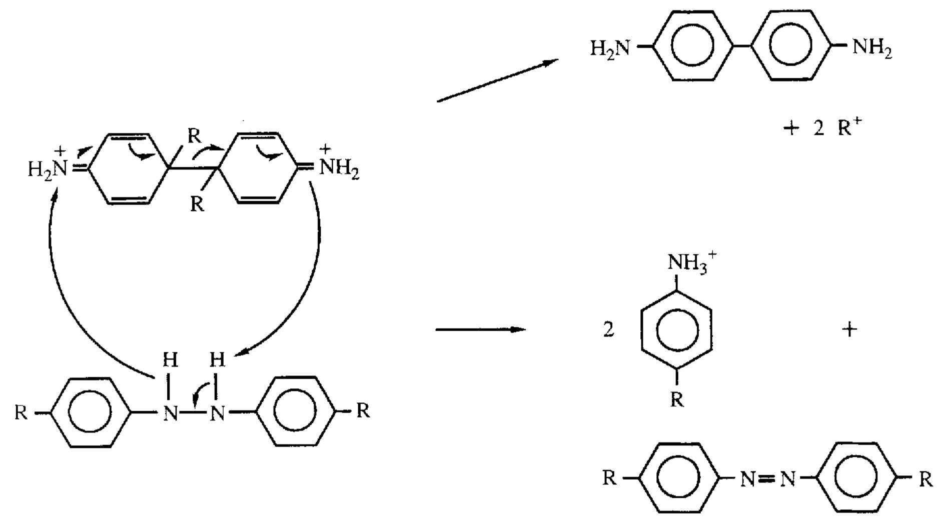
The puzzle of the mechanism of rearrangement was magnified in the mechanism of acid-catalyzed disproportionation [equation (5)]. In time, it was found that disproportionation had the kinetic character of the rearrangement which it accompanied. That is, all disproportionations were first order in hydrazoarene and either first or second order in acid, paralleling exactly the accompanying rearrangement.

It was evident, therefore, that an intermediate had to be formed in a rate-determining step which in subsequent fast steps could either go on to the rearrangement product or react with another molecule of hydrazoarene and lead to disproportionation. It was essential in disproportionation that the N—N bond be broken because that was the rate-determining step, but the parts must remain together, because evidence for free fragments was untenable.[18-22] For some years it seemed that the only viable intermediate must be a π-complex. Disproportionation was formulated in that way (Scheme 3) by Dewar as early as 1949.[14]

Later, however, disproportionation was fitted to the PTS theory with the proposal that a quinonoidal intermediate could be formed in the rate-determining step, and in fast steps either continue to rearrangement or be reductively cleaved by a second molecule of hydrazoarene. This idea is shown with a *p*-quinonoid intermediate in Scheme 4,[36] but *o*-quinonoids could serve also.[37]



Scheme 3

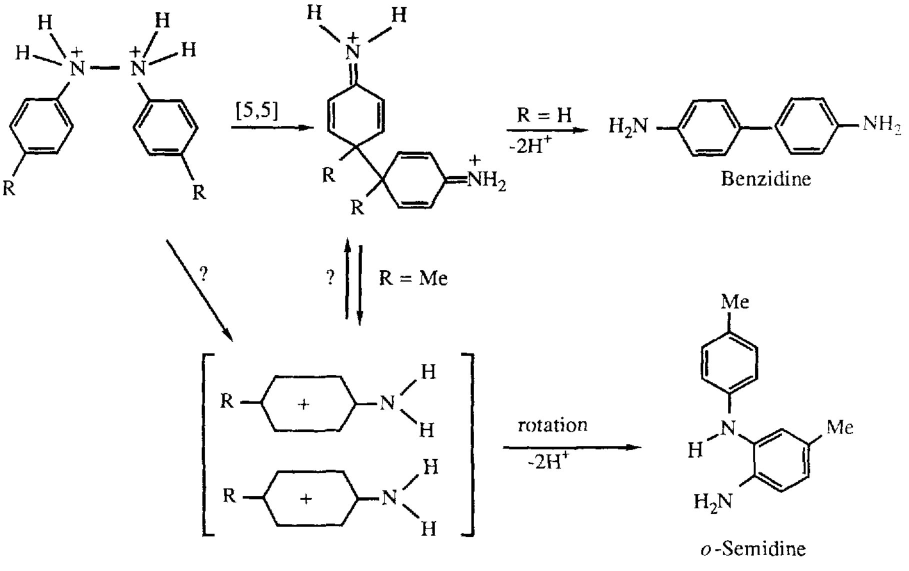


Scheme 4

The essential difference between the π-complex and PTS theories was never stated explicitly during the days of controversy. That difference was that in the π-complex theory all rearrangements had to go in two major steps (formation of a π-complex and conveyance to product) whereas in the PTS theory all rearrangements had to be concerted. This rate-process difference applied also to disproportionation. In the π-complex theory an intermediate was formed by breaking the N—N bond, and was reduced in a fast subsequent step. In the PTS theory an intermediate was formed in a concerted way, and only thereafter did the redox cleavage occur. As far as I am aware the concept of concertedness and its implications in these reactions were never brought explicitly to light by workers in the field during the period of controversy.

In 1950, recognizing the invalidity of a monoprotonated π-complex[13] in the rearrangement of hydrazobenzene, and believing that π-complex formation from diprotonated hydrazobenzene was less plausible, Hammond and Shine proposed that the new bonds of the products of rearrangement are partially formed before the old bond is broken,[15] in a manner similar to the suggestions of Robinson[3] and Hughes and Ingold.[4] This is the language of concerted reactions, but the enunciation and clarification of the concepts of concerted and non-concerted reactions were still more than a decade away.

The earliest proposal that the benzidine rearrangement might be a concerted, [5, 5]-sigmatropic rearrangement was by Fräter and Schmid. From Schmid's laboratory in those years came detailed and elegant work on the Claisen rearrangements. Frontier molecular orbital (FMO) treatment was applied in some detail to Claisen rearrangements by Schmid and coworkers,[38,39] and the possibility that examples of [5, 5]-sigmatropic rearrangements in positively charged systems might be found in benzidine rearrangements was also pointed out.[40] Curiously, Fräter and Schmid gave no consideration to the application of FMO treatment to the other types of hydrazoarene rearrangements. FMO theory was such that if benzidine formation was an allowed pericyclic process, the diphenyline and *o*-semidine rearrangements, by the same reasoning, could not be suprafacially concerted. I pointed out these consequences of FMO treatment in 1973 but, somewhat shortsightedly then, wrote that 'at this stage it does not seem useful to classify some of the rearrangements as sigmatropic shifts and leave others in limbo.'[20a] The portent for viewing benzidine rearrangements in a more global way was recorded first, however, by Alder, Baker and Brown,[41] who wrote: 'The benzidine rearrangement is apparently a [5,5]-shift, though, when the *para*-positions of the hydrazobenzene are blocked, other products (e.g. the *ortho*-semidine) are formed by rearrangements which are formally forbidden to be concerted. Probably an intermediate is formed the two halves of which can rotate before collapsing to give the various products and which probably lives long enough to forget its origins in orbital symmetry terms. The bonding in the intermediate is still uncertain and will probably vary according to whether it is diprotonated (Scheme 5) or mono- or un-protonated'. This cogent view of benzidine rearrangements was completely overlooked, it seems, in later works.



Scheme 5

An approach for distinguishing between concerted and two-step mechanisms of benzidine rearrangements with measurements of heavy-atom kinetic isotope effects (KIE) was begun at Texas Tech University in 1976. Initially, attention was turned to N—N bond breaking in the rearrangement of hydrazobenzene (**1**) itself, and it was found by isotope-ratio mass spectrometry[42] that there was a nitrogen KIE at about 2% for the disappearance of **1**.[34] It was not possible at that time to measure the KIE for the formation of each product. This was accomplished later, not only for nitrogen but also for carbon isotopes. In the later work KIE of stable isotopes were measured by whole-molecule-ion mass spectrometry (WMIMS),[43] and of ^{14}C, eventually, by scintillation counting. As the KIE work progressed, and with the availability of modern isotope-ratio mass spectrometers, it became possible to measure nitrogen KIE by combustion-isotope-ratio mass spectrometry on unenriched compounds to supplement the measurements by WMIMS on their enriched analogues. In the course of a few years examples of ^{15}N, ^{13}C, ^{14}C and ^{2}H KIE were assembled from which a rational view of the benzidine rearrangements could at last be formulated. The rearrangements are sigmatropic ones. In principle, therefore, as pointed out by Alder, Baker and Brown, some can and some cannot be concerted. The KIE data which we have gathered are in line with these expectations. Where a rearrangement can be concerted the KIE data (in all cases but one) are consistent with a concerted rearrangement. Where a rearrangement cannot be suprafacially concerted the KIE data are in accord with a non-concerted process. Our KIE results are summarized briefly below.

In the case of hydrazobenzene (**1**) itself, KIE were measured for the rearrangement of [^{15}N, ^{15}N′]-**1**, [4,4′-$^{13}C_2$]-**1**, [4-^{14}C]-**1**, [2,2′6,6′-$^{13}C_4$]-**1** and [4,4′-$^{2}H_2$]-**1**. The nitrogen and carbon KIE were measured for each product, benzidine (**2**) and diphenyline (**3**) [equation (1)]. The deuterium KIE could be measured only for the disappearance of hydrazobenzene and not for the formation of each product. The results are listed in Table 1. The nitrogen and carbon data show substantial KIE for bond breaking and bond forming for **2**. These results mean that stretching of the N—N and forming of the C—C bond are parts of the same transition structure, that is, that the 4,4′-quinonoid intermediate, which precedes and leads on rapidly to benzidine (**2**), is formed in a concerted way. Benzidine formation is thus classifiable as a [5, 5]-sigmatropic rearrangement. In contrast, the formation of diphenyline (**3**) is characterized by a substantial KIE for breaking the N—N bond but with no KIE for forming the C—C bond. In that case, N—N bond stretching is part of the transition structure, whereas C—C bond forming comes later. The results are not consistent with a concerted rearrangement, which is what one now expects for what is formally a [3, 5]-sigmatropic shift. The deuterium KIE reflect the secondary deuterium isotope effect for making the major product (**2**) in a concerted way; that is, in going from sp^2 hybridization in **1** toward sp^3 bonding in the quinonoid intermediate that leads on to **2**. As for the $^{13}C_4$ KIE, the value for **2** can only serve as a control of precision, and indicates that there is no KIE for forming **3**, a result consistent with those obtained with labeling in the *para* positions.

These heavy-atom KIE are small, but of the expected magnitudes. Cut-off-type calculations for simplified models of the transition structures for forming **2** and **3** gave, in fact, KIE close to the measured values.[35]

Rearrangement of hydrazobenzene is a two-proton case. KIE were measured, therefore, for the formation of a benzidine by a one-proton rearrangement, namely of 2,2′-dimethoxyhydrazobenzene [**10**, equation (7)].[45] The KIE results for the formation of product **11** from [^{15}N, ^{15}N′]-**10** and [4,4′-$^{13}C_2$]-**10** were 1·0289 and 1·0286, respectively,

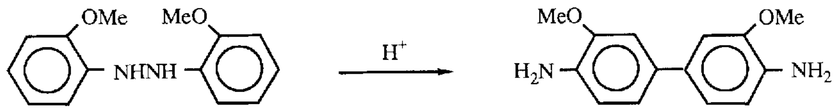
Table 1. KIE for the acid-catalyzed rearrangement of hydrazobenzene into benzidine (**2**) and diphenyline (**3**)

	KIE		
Label	**2**	**3**	Reference
^{15}N,^{15}N′ [a]	1·0222	1·0633	35
4,4′-^{13}C [a]	1·0209	1·0006	35
4-^{14}C	1·0284	1·0011	35
2,2′,6,6′-^{13}C	0·9945 [b]	0·9953 [c]	44
4,4′-^{2}H [a]	0·962		35

[a] For two atoms.

[b] Since the *para* positions were not labeled, there cannot be a KIE for forming **2**, and this number must be considered to be 1·000.

[c] Considered to be the same, experimentally, as for **2**.

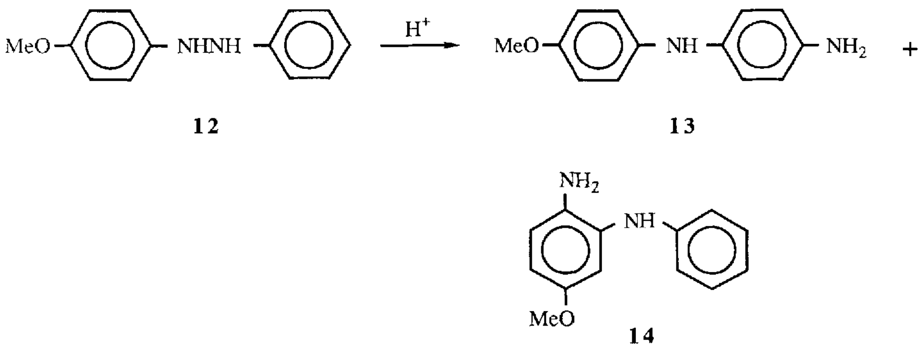


(7)

10 **11**

showing that this was a [5, 5]-sigmatropic rearrangement, too. Once again, an inverse secondary deuterium KIE for the disappearance of hydrazoarene was found, 0·929 for $[4,4'\text{-}{}^{2}H_{2}]$-**10**.

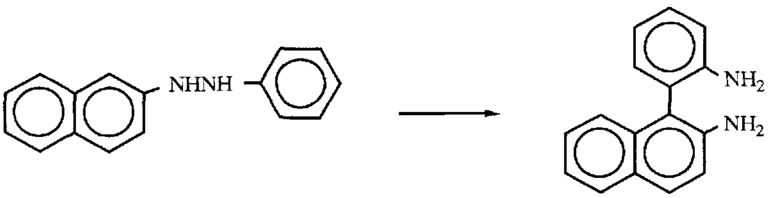
Rearrangement of 4-methoxyhydrazobenzene (**12**) into the *p*- (**13**) and *o*-semidine (**14**) [equation (8)] occurs by one-proton catalysis. The formation of **13** and **14** from $[{}^{15}N, {}^{15}N']$-**12** resulted in KIE of 1·0296 and 1·074, respectively, showing that in each case stretching of the N—N bond occurred in the transition structure. Formation of **13** from $[4\text{-}{}^{14}C]$-**12** resulted in a carbon KIE of 1·039.[46] The nitrogen and carbon results showed that the *p*-semidine rearrangement was a [1, 5]-sigmatropic shift.



12 **13** **14**

(8)

o-Benzidine rearrangements are, in principle, [3, 3]-sigmatropic shifts. That this is the case, in fact, was shown with the rearrangements of 2,2′-hydrazonaphthalene [**8**, equation (4)] and *N*-2-naphthyl-*N*′-phenylhydrazine [**15**, equation (9)]. That is, the one-proton catalyzed formation of **9** from $[{}^{15}N, {}^{15}N']$-**8** and $[1,1'\text{-}{}^{13}C_{2}]$-**8** had KIE of 1·0904 and 1·0086, respectively, indicative of a concerted rearrangement in an unsymmetrical transition structure.[47]



(9)

15 **16**

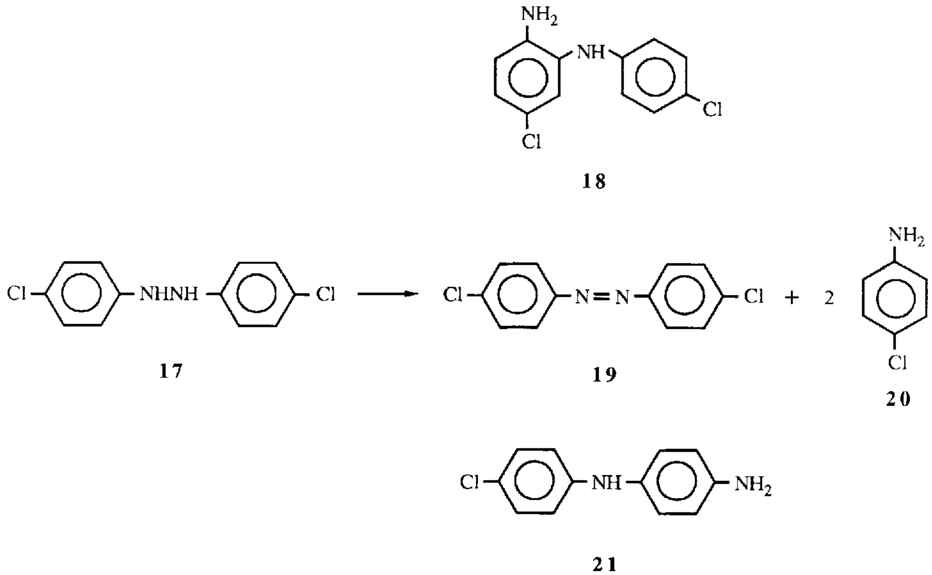
Table 2. KIE for the acid-catalyzed rearrangement of *N*-2-naphthyl-*N*′-phenylhydrazine (**15**)

Label	KIE	Reference
$^{15}\mathrm{N}$, $^{15}\mathrm{N}'$ [a]	1·0434	48
$^{14}\mathrm{N}$, $^{15}\mathrm{N}'$ [b]	1·0196	48
$2'$-$^{14}\mathrm{C}$	1·0287	48
$2'$-$^{13}\mathrm{C}$ [b]	1·0176	48
$2',6'$-$^{13}\mathrm{C}_2$	1·0177	44

[a] For two atoms.
[b] With unenriched **15**.

Rearrangement of **15** into **16** occurs by two-proton catalysis. In this case, nitrogen and carbon-13 KIE were measured with enriched (WMIMS) and unenriched (isotope ratio) **15**. The results are listed in Table 2, and are clearly indicative of a [3, 3]-sigmatropic rearrangement.

All of these rearrangements had KIE which are consistent with what one would expect of sigmatropic shifts. Among benzidine rearrangements, the *o*-semidine one is a [1, 3]-sigmatropic shift and is, in principle, 'forbidden' from being suprafacially concerted. We were unable to find in the literature an *o*-semidine rearrangement which was ideally suited for KIE measurements. We chose the rearrangement of 4, 4′-dichlorohydrazobenzene (**17**) into the *o*-semidine (**18**), knowing that disproportionation into 4, 4′-dichloroazobenzene (**19**) and 4-chloroaniline (**20**) also occurred. We found, though, that a *p*-semidine (**21**) rearrangement, already known to occur with the ejection of one of the *para*-chlorine atoms (Scheme 6), occurred to about the same extent as the *o*-semidine rearrangement. Therefore, KIE were measured for each of the three reactions.[49,50] The results are given in Table 3 for the formation of *o*- and *p*-semidines. They show that there is a nitrogen KIE for each rearrangement but a carbon KIE for neither, that is, neither the *o*- nor *p*-semidine rearrangement is found to be concerted.



Scheme 6

Table 3. KIE for the acid-catalyzed rearrangement of 4,4′-dichlorohydrazobenzene (**17**) into an *o*-semidine (**18**) and *p*-semidine (**21**)[49]

Label	KIE **18**	KIE **21**
^{15}N, $^{15}N'$ [a]	[b]	1·0282
^{14}N, $^{15}N'$ [c]	1·0155	1·0162
2-^{14}C	0·9989	[b]
4-^{14}C	1·0027[d]	1·0029
4,4′-$^{13}C_2$ [a]	0·9993[d]	0·9934

[a] For two atoms.
[b] Not measured.
[c] From unenriched **17**.
[d] Labeling could not result in a KIE for this product. Mass measurements were made and are expressed as a KIE to serve only as a guide to precision in measurements with **21**.

Collectively, therefore, all but one of the KIE which we have measured for acid-catalyzed benzidine rearrangements are consistent with what one expects of sigmatropic rearrangements. The only exception was the *p*-semidine (**21**) formation from **17** which does not exhibit a KIE, but even this case is not a contradiction of what one might expect.

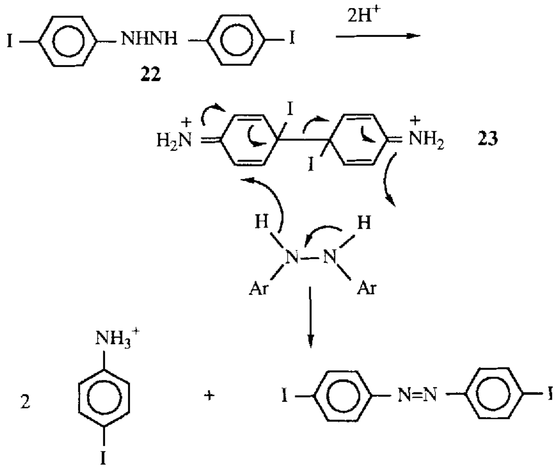
The reasons for saying this are two-fold. One reason is that a rearrangement does not have to be concerted just because the principles of orbital symmetry allow for concertedness. The other reason lies in the peculiarities of bond-forming KIE. Fry has pointed out that if valid, they are usually greater than unity, but in particular circumstances they may be valid, yet less than or, by cancellation of effects, equal to unity.[51]

Earlier, reference was made to thermal benzidine rearrangements. These are not so common as the acid-catalyzed rearrangements. The 'cleanest' is that of 2,2′-hydrazonaphthalene (**8**) into 2,2′-diamino-1,1′-binaphthyl [**9**, equation (4)].[31] KIE were measured for this rearrangement and were 1·0611 for [^{15}N, $^{15}N'$]-**8** and 1·0182 for [1,1′ $^{13}C_2$]-**8**.[47] Clearly, this rearrangement is none other than a [3,3]-sigmatropic shift.

Let us now turn to the problem of acid-catalyzed disproportionation. A distinction between the intervention of a quinonoidal or π-complex intermediate was made with KIE measurements in the disproportionation of 4,4′-diiodohydrazobenzene (**22**).[52] Substantial KIE were found for nitrogen and *para*-carbon labeling in the disproportionation of **22**. The results for [^{15}N, $^{15}N'$]-**22**, [4,4′-$^{13}C_2$]-**22** and [4-^{14}C]-**22** were 1·0367, 1·0230 and 1·0450, respectively. There is no question, it seems that the N—N bond is breaking and the 4,4′ bond is forming in the formation of the required intermediate. The only choice available for that, then, is the quinonoidal one (**23**, Scheme 7). A π-complex cannot be the intermediate in this reaction.

In contrast with disproportionation of **22**, disproportionation of **17** (Scheme 6) exhibited nitrogen but neither *ortho*- nor *para*-carbon KIE.[49] In this case, therefore, the nature of the intermediate in disproportionation is not clearly identifiable. Since bond-forming KIE were not found for either *o*- or *p*-semidine formation, either the *o*- or *p*-quinonoid intermediate could serve for disproportionation. Our product analyses implicated the *p*-quinonoid.[49]

Insofar as the mechanism of the benzidine rearrangements is concerned, then, we have, in



Scheme 7

a sense, come full circle. It is clear that Banthorpe, Hughes and Ingold were wrong in clothing all of the rearrangements in the same garb. It is also clear that Dewar was wrong in ascribing π-complex intermediates to them all, particularly the neutral class. On the other hand, in that the PTS theory called for concerted rearrangements it was, in some types, correct. Those types, of course, are the ones which comply with the dictates of conservation of orbital symmetry. The PTS theory was formulated before the popularization of the concepts of pericyclic reactions and it is a coincidence, therefore, that its characteristics are borne out in some cases. Application of the PTS theory to thermal rearrangements had a sense of reality initially, because the rearrangements occurred better in polar (alcohol) than in non-polar (benzene) solvents.[31] Insofar as concertedness is concerned, the PTS theory was correct, but again only by coincidence. What about the 'forbidden' cases, that is, the diphenyline and *o*-semidine rearrangements? How can we accommodate intramolecularity with non-concertedness? It may well be that in these cases Dewar was correct, in that a π-complex intermediate is formed. The distinction in energetics between a concerted and π-complex mechanism may, in fact, be a fine one, in that the π-complex represents a shallow depression in the energy surface of a 'forbidden' rearrangement. Perhaps we can rest with the description given by Alder, Baker and Brown of an intermediate which has forgotten its origin in orbital symmetry terms.[41]

When we look back on the two theories of the 1960s, therefore, we see now that neither was wholly right, yet neither was wholly wrong. In particular, the π-complex theory, which was intrinsically very attractive but suffered from the exuberance of its initial dressings, may have been rehabilitated in part by the new experimental findings. Perhaps the benzidine rearrangements are now (or should we say 'for the while'?) settled. In retrospect, Dewar's innovative π-complex idea stimulated a great deal of excitement, challenge and research.

One last possibility should be dealt with. Can the nitrogen KIE which we have reported represent equilibrium KIE for π-complex formations, and the carbon KIE represent the rate-determining product-forming steps? The magnitude of equilibrium KIE for N—N bonds has, as far as we know, not been measured. However, the above possibility can be dismissed because were it correct there should be no variance in the nitrogen KIE for each product in reactions in which more than one product is formed, e.g. the rearrangements of hydrazobenzene and

4-methoxyhydrazobenzene. Further, we could expect to find bonding KIE in all rearrangements, and it would be surely more than coincidence could bear to find KIE in only those cases which were also consistent with concerted rearrangements.

ACKNOWLEDGEMENTS

Research in benzidine rearrangements at Texas Tech has received lengthy support from the Robert A. Welch Foundation (Grant D-028) and the National Science Foundation. To both Foundations and my many coworkers I express my gratitude. This paper was written in part during the tenure of an Alexander von Humboldt US Senior Scientist Award. I thank the AvH Foundation for the award and the Institut für Organische Chemie, Universität Hamburg, for hospitality. I thank Dr. Roger Alder and Wiley–Interscience for permission to quote from and reproduce Scheme 5 from the book *Mechanism in Organic Chemistry*. I thank Mrs. Jane Bradley and Mr. Donald T. Robertson for making the drawings.

REFERENCES AND NOTES

1. J. D. Cheng and H. J. Shine, *J. Org. Chem.* **39**, 336–340, 2835–2838 (1974); D. H. Bae and H. J. Shine, *J. Org. Chem.* **46**, 4700–4704 (1981).
2. J. Jacobson, *Justus Liebigs Ann. Chem.* **428**, 76–121 (1922).
3. R. Robinson, *J. Chem. Soc.* 220–240 (1941).
4. E. D. Hughes and C. K. Ingold, *J. Chem. Soc.* 608–613 (1941).
5. C. K. Ingold and H. V. Kidd, *J. Chem. Soc.* 984–988 (1933).
6. M. J. S. Dewar, *Nature (London)* 784 (1945). The detail of this description was not repeated in subsequent publications. There is a problem inherent in the descriptions of parts A and B. A can be aniline and B a cation, or A can be a cation radical and B a radical, but B cannot be a cation radical, while A is an aniline derivative.
7. J. P. van Loon, *Recl. Trav. Chim. Pays-Bas* **23**, 62–97 (1904).
8. No reference to van Loon's work is to be found in the 'mechanistic' papers of the 1940s, except for one by Carlin.[9] Carlin investigated the products of rearrangement of 3,3′,5,5′-tetramethylhydrazobenzene, to find if such substituents would affect the structure of the products of rearrangement. In fact, Carlin found a benzidine type-to-diphenyline type ratio of about 3 : 2 and contrasted that with van Loon's report[7] of a benzidine-to-diphenyline ratio of about 4 : 1. This difference in ratios was to be used later by Dewar[10] as support for the π-complex theory, in that the substituents were said to lead to rotation to a less hindered, diphenyline-type conformation in the π-complex. Unfortunately, it seems now, Carlin commented on van Loon's product ratios but not on the kinetics, a subject which he was to take up and compare with van Loon's data only later.[11] It is interesting to speculate that had he done so, or had Dewar gone back to van Loon's paper, the path of the π-complex theory may have been smoother. Further, it is probable that, in that case, neither the present writer nor G. S. Hammond would have entered the benzidine mechanism fray.

   Whether one or two protons was involved in a rearrangement must have been in the minds of Hughes and Ingold, however, because they wrote that 'acid catalysis shows that one or more adding protons are present in the transition state of the rearrangement,' and that 'a nearby proton (at least one) disturbs the electronic system of the benzidine (*sic*) molecule.' It may be that at that time Hughes and Ingold were not much further interested in a more precise kinetic description of acid catalysis because they deliberately excluded prior protonation from the mechanistic pathway.

   What is more surprising about the situation in the early 1940s is that it was not so long before that time that Jacobson published his exhaustive summary of benzidine rearrangements.[2] All of the theorists must have been aware of the summary, and some even quoted it.[3,4] Yet, it seems, none of the later workers read the last and poignantly honest paragraph of Jacobson's paper. Therein, Jacobson points out that one should expect to obtain a picture of the rearrangements above all through kinetic investigations, which he, himself, had had to forego owing to 'the lack of time and

training.' However, Jacobson noted that in 1904 van Loon had reported kinetic investigations from Holleman's laboratory. Perhaps because we was not a kineticist Jacobson did not report van Loon's result, crude as it was, of second-order acid catalysis. In any case, the theorists of the 1940s, and Hammond and Shine later, missed Jacobson's lead entirely.

There is yet another strange turn in this historical pathway. In 1933 Ingold and Kidd demonstrated that the benzidine rearrangement was intramolecular.[5] In that work they also encountered, for the first time, the acid-catalyzed disproportionation reaction which later became so important mechanistically. Ingold and Kidd refer (although with an erroneous page number) to van Loon's paper,[7] but not to its kinetics discovery. Instead, conscious of the novelty of their finding the acid-catalyzed disproportionation, they cite van Loon as having also observed, apparently for the first time, the formation of a mononuclear amine in the absence of a reducing agent. Even more strange is the fact that Ingold and Kidd do, indeed, refer to rate measurements as having been made by Holleman and van Loon. However, the reference is not to van Loon's comprehensive paper but to an earlier one in a less accessible journal [A. F. Holleman and J. P. van Loon, *Proc. Konl. Akad. Wetensch.* (Amsterdam), **6**, 262–267 (1903)]. In this report Holleman is explicit about van Loon's discovery of second-order hydrogen ion kinetics. It is remarkable therefore that Ingold then had at hand two reports of van Loon's work, only to lose track of them, apparently, later. It is quite clear from Ingold's later writings that, until, Hammond and Shine rediscovered the second-order acid kinetics in 1950, he accepted that all benzidine rearrangements were first order in acid.

9. R. B. Carlin, *J. Am. Chem. Soc.* **67**, 928–933 (1945).
10. M. J. S. Dewar, *J. Chem. Soc.* 406–408 (1946).
11. R. B. Carlin, R. G. Nelb and R. C. Odioso, *J. Am. Chem. Soc.* **73**, 1002–1007 (1951).
12. E. Biilmann and J. H. Blom, *J. Chem. Soc.* **125**, 1719–1731 (1924).
13. M. J. S. Dewar, *J. Chem. Soc.* 777–781 (1946). In this paper Dewar described the use of Bindschedler's Green for measuring concentrations of hydrazoarenes, a technique that was to make kinetic work so easy for later experimenters.
14. M. J. S. Dewar, *The Electronic Theory of Organic Chemistry*, Oxford University Press, Oxford, 1949, pp. 233–240.
15. G. S. Hammond and H. J. Shine, *J. Am. Chem. Soc.* **72**, 220–221 (1950). Measuring the kinetics of disappearance of hydrazobenzene was made easy by being able to use Dewar's method with Bindschedler's Green. We were unaware of van Loon's earlier work,[7] and we were unaware also that work was underway in Carlin's laboratory which was to provide the same kinetic answer.[11] Carlin and coworkers measured rates of rearrangement by spectroscopic analyses of mixtures of hydrazoarene and products.[11,16,17] This method had the advantage of allowing for comparison of rates for each product in cases in which more than one product was formed, but was much more tedious and time consuming than Dewar's method with Bindschedler's Green. Van Loon[7] measured rates of rearrangement with saturated solutions of hydrazobenzene in 50% and (mostly) 15% ethanol in water. The amount of benzidine formed at timed intervals was assayed by precipitating and weighing its hydrogensulfate salt. The total amount of product (benzidine plus diphenyline) formed at the chosen times was then computed from earlier determination of the percentage of benzidine formed at total conversion. Diphenyline was not isolated but was assumed to represent the balance of the conversion. Van Loon fitted his product/time data to a rate expression for an assumed second-order acid dependence and obtained remarkably good constancy in the values of the rate constant. In this way, first-order hydrazobenzene and second-order acid dependences were established. Thus, in contrast, the method of measuring the rate of disappearance of hydrazoarene with Bindschedler's Green was a major help to kineticists.
16. (a) R. B. Carlin and R. C. Odioso, *J. Am. Chem. Soc.* **76**, 100–104 (1954); (b) R. B. Carlin and R. C. Odioso, *J. Am. Chem. Soc.* **76**, 2345–2349 (1954).
17. R. B. Carlin and G. S. Wich, *J. Am. Chem. Soc.* **80**, 4023–4033 (1958).
18. D. V. Banthorpe, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.* 2864–2901 (1964).
19. H. J. Shine, *Aromatic Rearrangements*, Elsevier, New York, 1967, pp. 126–179
20. (a) H. J. Shine, *MTP Int. Rev. Sci., Org. Chem. Ser. I*, **3**, 79–84 (1973); (b) *Ser. II*, **3**, 100–110 (1976).
21. D. V. Banthorpe, *Top. Carbocycl. Chem.* **1**, 1–62 (1969); *Chem. Rev.* **70**, 295–322 (1970). In the latter review Banthorpe criticizes the role of π-complexes in the benzidine rearrangement.
22. R. A. Cox and E. Buncel, in S. Patai (Ed.), *The Chemistry of the Hydrazo, Azo, Azoxy Groups*, Wiley, New York, 1975, pp. 777–805.

23. M. J. S. Dewar, *Annu. Rep. Chem. Soc.* **48**, 112–135 (1951).
24. M. J. S. Dewar, *Kekulé Symposium on Theoretical Organic Chemistry, London, 1958*, Butterworths, London, 1958, pp. 179–208.
25. M. J. S. Dewar, in P. de Mayo (Ed.), *Molecular Rearrangements, Part 1*, Interscience, New York, 1963, pp. 295–344.
26. C. A. Bunton, C. K. Ingold and M. M. Mhala, *J. Chem. Soc.* 1906–1913 (1957).
27. H. J. Shine and J. T. Chamness, *Tetrahedron Lett.* 641–644 (1963).
28. G. Friebel and B. Rassow, *J. Prakt. Chem.* **63**, 444–465 (1901).
29. H. J. Shine and J. P. Stanley, *J. Org. Chem.* **32**, 905–910 (1967).
30. M. J. S. Dewar and A. P. Marchand, *Annu. Rev. Phys. Chem.* **16**, 338–346 (1965).
31. H. J. Shine, *J. Am. Chem. Soc.* **78**, 4807–4809 (1956); H. J. Shine and R. L. Snell, *Chem. Ind. (London)*, 706–707 (1957); H. J. Shine and J. C. Trisler, *J. Am. Chem. Soc.* **82**, 4054–4058 (1960); H. J. Shine, F. T. Huang and R. L. Snell, *J. Org. Chem.* **26**, 380–383 (1961).
32. (a) Z. T. Allan, *Tetrahedron Lett.* 4225–4228 (1971); *Monatsh. Chem.* **106**, 429–436 (1975); *Justus Liebigs Ann. Chem.* 705–709 (1978); (b) M. E. Lupes, *Rev. Roum. Chim.* **17**, 1253–1260 (1972); (c) G. A. Olah, K. Dunne, D. P. Kelly and Y. I. Mo, *J. Am. Chem. Soc.* **94**, 7438–7447 (1972); (d) A. Heesing and U. Schinke, *Chem. Ber.* **110**, 3119–3323 (1977).
33. D. V. Banthorpe, *Tetrahedron Lett.* 2707–2710 (1972).
34. H. J. Shine, G. N. Henderson, A. Cu and P. Schmid, *J. Am. Chem. Soc.* **99**, 3719–3723 (1977).
35. H. J. Shine, H. Zmuda, K. H. Park, H. Kwart, A. G. Horgan and M. Brechbiel, *J. Am. Chem. Soc.* **104**, 2501–2509 (1982).
36. D. V. Banthorpe, A. C. Cooper and C. K. Ingold, *Nature (London)*, **216**, 232–235 (1967).
37. D. V. Banthorpe and J. Winter, *J. Chem. Soc., Perkin Trans. 2* 868–873 (1972).
38. H.-J. Jansen and H. Schmid, *Chem. Brit.* 111 (1969); *Chimia* **24**, 89–99 (1970).
39. Gy. Fräter, A. Habich, H.-J. Hansen and H. Schmid, *Helv. Chim. Acta* **52**, 335–361 (1969).
40. Gy. Fräter and H. Schmid, *Helv. Chim. Acta* **53**, 269–290 (1970).
41. R. W. Alder, R. Baker and J. M. Brown, *Mechanism in Organic Chemistry*, Wiley–Interscience, London, 1971, pp. 273 and 274.
42. The idea of distinguishing between the π-complex and PTS theories by measuring KIE was first mentioned to Prof. C. A. Bunton in a 'corridor' discussion at a meeting of the American Chemical Society. At that time facilities for measuring mass ratios were not available at Texas Tech University, and the research idea may have remained an idea only. However, Professor Bunton suggested that the help of Professor A. N. Bourns and his isotope-ratio mass spectrometry group at McMaster University be solicited. Through Professor Bourns the collaboration of his former coworker, Dr Peter Schmid, was enlisted. Schmid, then at the National Research Council, Ottawa, was able to obtain leave from the NRC to make the isotope-ratio measurements in Hamilton.
43. The possibility of measuring KIE of stable isotopes by WMIMS and hence not having to go through conversions into N_2 and CO_2 for isotope-ratio mass spectrometry was suggested by my friend of many years, the late Professor Harold Kwart. Once again, facilities for making the measurements (a quadrupole mass spectrometer and a computer to gather and treat statistically thousands of selected-ion abundance measurements) were then not available at Texas Tech University. Measurements were carried out in Professor Kwart's laboratory and, for a while after his death, in the laboratory of Professor Joseph San Filippo, Jr, without whose help continued work would have been impossible.
44. L. Kupczyk-Subotkowski, H. J. Shine, W. Subotkowski and J. Zygmunt, *Gazz, Chim. Ital.* **117**, 513–516 (1987).
45. H. J. Shine, K. H. Part, M. L. Brownawell and J. San Filippo, Jr, *J. Am. Chem. Soc.* **106**, 7007–7082 (1984).
46. H. J. Shine, H. Zmuda, H. Kwart, A. G. Horgan and M. Brechbiel, *J. Am. Chem. Soc.* **104**, 5181–5184 (1982).
47. H. J. Shine, E. Gruszecka, W. Subotkowski, M. L. Brownawell and J. San Filippo, Jr, *J. Am. Chem. Soc.* **107**, 3218–3223 (1985).
48. H. J. Shine, L. Kupczyk-Subotkowska and W. Subotkowski, *J. Am. Chem. Soc.* **107**, 6674–6678 (1985); **109**, 1286 (1987).
49. E. S. Rhee and H. J. Shine, *J. Am. Chem. Soc.* **108**, 1000–1006 (1986); **109**, 5052 (1987).
50. E. S. Rhee and H. J. Shine, *J. Org. Chem.* **52**, 5633–5636 (1987).
51. A. Fry, in C. J. Collins and N. S. Bowman (Eds), *Isotope Effects in Chemical Reactions*, Van Nostrand Reinhold, New York, 1970, pp. 364–414.
52. H. J. Shine, J. Habdas, H. Kwart, M. Brechbiel, A. G. Horgan and J. San Filippo, Jr, *J. Am. Chem. Soc.* **105**, 2823–2827 (1983).