[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

THE REPULSION OF ATOMIC KERNELS AS A FACTOR IN ORGANIC REARRANGEMENTS

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Although the repulsion of the atomic kernels is an obvious factor[1] in the stability of molecules, its importance in organic chemistry does not seem to be fully appreciated. In the recent monograph on Molecular Rearrangements by Porter,[2] there are so many examples of the influence of the inter-kernel repulsions, that it appears desirable to formulate a statement which will be of assistance in interpreting these complex organic reactions.

The energy of the molecule is, of course, the sum of the energies of the repulsions and attractions of the electrons and atomic kernels and at present it is quite impossible to evaluate all these energies. Indeed, our one bit of quantitative information is the energy of repulsion of the atomic kernels. In this case, since these kernels are small in comparison to the interatomic distances, the energy of repulsion between two kernels of charges e and e', separated by a distance, d, is $E = ee'/d$. The interatomic distances are capable of determination from crystal structure data and as the kernel is, by definition, the atom minus the valence electrons, its charge is equal to the number of valence electrons possessed by the neutral atom.

The magnitude of this repulsive energy is very great, for example, that between carbon and nitrogen in aniline is over two million calories. In a stable molecule this repulsion is overcome by the mutual attractions of the kernels for the electrons or electron pairs of the two atoms, but it seems obvious that if any arrangement of the molecule is possible in which this repulsion force may be greatly decreased and at the same time satisfy equally well the electron affinities of all the atoms, such a rearrangement might take place. For example, in the change of methylaniline into *p*-toluidine, N—C and C—H bonds are changed to N—H and C—C bonds. In the resulting molecule the atoms all possess the same number of electrons which they had before the rearrangement but the energy of repulsion has been decreased by approximately 400,000 cal. The free energy of the change is very much less than this, so there must also be a decrease in the energy of the bonding electrons. Although the latter cannot be calculated, it seems probable that it should always be less than the decrease in the repulsion energy.

In order to test this assumption, a survey has been made of all the re-

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[1] See Pauling and Hendricks, THIS JOURNAL, **48**, 641 (1926); Latimer and Rodebush, *ibid.*, **42**, 1419 (1920).

[2] Porter, "Molecular Rearrangements," The Chemical Catalog Co., Inc., New York, **1928**.

arrangements listed by Porter and the reactions are classified according to the bonds broken and formed. The values used in calculating the increase or decrease of the repulsion energies are summarized in Table I. These energies are based upon interatomic distances determined by x-ray diffraction data and molecular moments from band spectra data. It is to be expected that each type of bond should be only approximately constant in various compounds and in general variations of 10 and 15% in the interatomic distances are found. The values for the interatomic distances which have been employed are taken from summaries by Pauling,[3] Huggins[4] and Birge.[5]

The various types of rearrangements and their repulsion energies are summarized in Table I. In the following discussion the numbers refer to the types as listed in Table II.

TABLE I

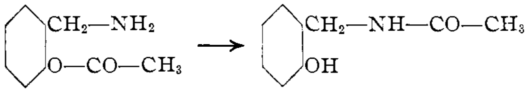
REPULSION ENERGIES OF ATOMIC KERNELS IN VARIOUS BONDS[a]

Bond	Dist. bet. atomic centers, Å.	Repulsion energy, kilocal.	Bond	Dist. bet. atomic centers, Å.	Repulsion energy, kilocal.
C—H	1.20	550	N—N	1.40	2950
C—C	1.52	1700	N=N	1.21	3400
C=C	1.47	1750	N—O	1.35	3650
C—N	1.46	2250	N=O	1.20	4100
C=N	1.20	2750	N—S	1.65	3000
C—O	1.41	2800	N—Cl	1.64	3500
C=O	1.29	3050	N—Br	1.79	3200
C—S	1.71	2300	O—H	1.05	940
C—Cl	1.70	2700	O—O	1.30	4550
C—Br	1.85	2500	O=S	1.56	3800
N—H	1.15	715	O—Cl	1.52	4550

[a] Instead of these values, as a rough approximation, applicable in most cases, the interatomic distances may be assumed constant and the energies expressed in terms of the product of the kernel charges. For example, in the N—C and C—H rearrangement to N—H and C—C given above $(5 \times 4) + (4 \times 1) = 24$ and $(5 \times 1) + (4 \times 4) = 21$. This decrease of 3 units corresponds to about 400 kilocal. in this example.

Rearrangements Taking Place with a Decrease in Repulsion Energy.—(1) The example of methylaniline has been given above. Other rearrangements of this type are methylenedi-*p*-tolylimide to diaminoditolymethane, ethylphthalimidoacetate to a derivative of oxycarbostyril, diacylanilides to acylamino ketones and N-acetylpyrrole to ∂-acetylpyrrole.

(2) There are a number of reactions similar to the following



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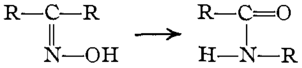
[3] Pauling, *Z. Krist.*, **67**, 377 (1928).

[4] Huggins, *Phys. Rev.*, **28**, 1086 (1926).

[5] Birge, "International Critical Tables," Vol. V, **1929**, p. 409.

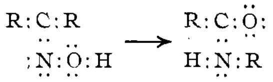
Other examples are: the ethyl ester of formanilide to ethylphenylformamide and the rearrangement of the triazoles.

(3) Many examples of the Beckmann rearrangement



$$\begin{array}{c} R-C-R \\ \| \\ N-OH \end{array} \longrightarrow \begin{array}{c} R-C=O \\ | \\ H-N-R \end{array}$$

It seems probable that these double bonds between carbon and the more electronegative atoms are not to be interpreted as two electron pairs, but rather as carbon with a coördination number of three, as in carbonate. However, the interatomic distances are less in the double bond and there is doubtless considerable distortion of the octet of the nitrogen and oxygen. The electron formula then would be

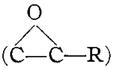


$$\begin{array}{c} R:C:R \\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H \end{array} \longrightarrow \begin{array}{c} R:C:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}: \\ H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}:R \end{array}$$

This interpretation is important in the generalization which we wish to draw later. Another example is the conversion of fluorenone oxime to phenanthridone.

TABLE II

CHANGE IN INTER-KERNEL REPULSION ENERGIES IN VARIOUS MOLECULAR REARRANGEMENTS

	Bonds rearranged	Energies in kilocal.
(1)	(C—N + C—H) to (N—H + C—C)	− 385
(2)	(O—C + N—H) to (O—H + N—C)	− 225
(3)	(C—C + N—O—H) to (C=O + H—N—C)	− 275
(4)	(=S=O + C—H) to (=S + C—O—H)	− 360
(5)	(O—C + =S) to (=O + S—C)	− 500
(6)	(O—C + C—H) to (O—H + C—C)	− 710
(7)	(N—Cl + C—H) to (N—H + C—Cl)	− 635
(8)	(C—N=C) to (C—C≡N)	− 550
(9)	(N—S + C—H) to (N—H + C—S)	− 535
(10)	(C—Br + N—Cl) to (C—Cl + N—Br)	− 100
(11)	(N—N + 2(C—H)) to (C—C + 2(N—H))	−2300
(12)	(N—N + C—H) to (N—H + C—N)	− 535
(13)	(N—O + C—H) to (C—O + N—H)	− 685
(14)	 to (R—C—C=O)	−2550
(15)	(C—S + ≡N) to (=S + =N—C)	− 50
(16)	(C—C′ + C″—C‴) to (C—C″ + C′—C‴)	0
(17)	(C—N + N′—H) to (C—N′ + N—H)	0
(18)	(C—X + C′—H) to (C′—X + C—H)	0
(19)	(C—C + —N) to (C—N= + C=)	+ 550
(20)	(N—C + =O) to (—N= + O—C)	+ 450

(4) The rearrangements of amine sulfoxides.

(5) Thioncarbamates to thiol derivatives.

(6) A great many examples of which the rearrangement of the allyl ethers is typical.

(7) The rearrangement of acyl halogen aminobenzene.
(8) The conversion of ethyl isocyanide to propionitrile.
(9) Several cases in the sulfonic acids and amides of sulfonic acids.
(10) The rearrangement of brominated benzenediazonium chloride.
(11) The benzidine type of rearrangement.
(12) Numerous cases of the nitroso-amines and hydrazines.

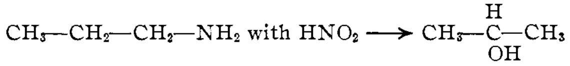
(13) One example is β-phenylhydroxylamine to *p*-aminophenol. Other examples are the rearrangements of the amine oxides and the conversion of quinoline by alkyl halides to carbinol bases.

(14) This change appears to be an intermediate step in some of the pinacol rearrangements. Although the definite formation of the intermediate ethylene oxide may not always occur in these reactions, the free bonds on the oxygen and carbon which result from the splitting off of water are potentially equivalent to the oxide formation. Other rearrangements essentially the same are benzil to benzilic acid and benzoin to diphenylacetic acid.

(15) The change of methyl thiocyanate to methyl isothiocyanate, $R—S—C \equiv N \longrightarrow R—N=C=S$. Although in the older bond theories of organic chemistry this change might be interpreted as involving a shift in the number of electrons on each atom, the probable electron formulas do not indicate that such is the case, that is, the structure is similar to that of carbon dioxide

$$R:\underset{..}{\ddot{S}}:C:\underset{..}{\ddot{N}}: \longrightarrow :\underset{..}{\ddot{S}}:C:\underset{..}{\ddot{N}}:R$$

Reactions Involving no Change in Repulsive Energy.—(16) There are a number of examples of shifts of carbon to carbon bonds. These often take place during reactions, that is, when the molecule is in a highly activated state, as in the following



$$CH_3—CH_2—CH_2—NH_2 \text{ with } HNO_2 \longrightarrow CH_3—\underset{OH}{\overset{H}{C}}—CH_3$$

As might be expected if the two possible forms have nearly the same energy the product is a mixture of the two forms. In some examples, however, symmetry and steric effects also doubtless play a part in determining the more stable form. Carbon to carbon shifts also occur in unsaturated compounds, the rearrangement giving forms which decrease the electrical moment of the molecule. An example of such a change is found in the reduction of methyl *tert.*-butyl ketone to tetramethylethylene.

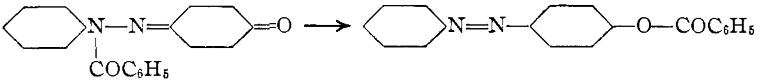
(17) One of the simpler examples is the change of $(NHR)(NR—NH_2)C=O$ to $(NHR)(NH—NHR)C=O$. Although this reaction involves no change in the kernel repulsions in the various bonds, it might be pointed out that the repulsion of the R group for all of the neighboring atoms appears to be decreased by this rearrangement.

(18) There are several examples of the shift of a halogen from one carbon to another.

Rearrangements Involving an Increase in the Repulsion Energy.—(19) Porter[6] considers that the best theory of the Hofmann and Curtius rearrangements is the formation of an intermediate compound containing an unsaturated nitrogen which then rearrange with the transfer of a carbon radical to the nitrogen. For example, R—CO—NHBr ⟶ R—CO—N ⟶ R—N=C=O, or in electron formulas, $R:\underset{:N:}{\underset{..}{C}}:\overset{..}{\underset{..}{O}}: \longrightarrow R:\overset{..}{\underset{..}{N}}:C:\overset{..}{\underset{..}{O}}:$. If this mechanism is correct the change involves an increase in the repulsion energies but it also involves a change in the number of electrons on the nitrogen, that is, it takes place because the more electronegative nitrogen will gain electrons at the expense of the carbon. However, there is a possibility that the first step is the interchange of the R and Br and in this case there is first a decrease in the repulsion energy.

In addition to the many examples of the Hofmann rearrangement, certain benzene-azo-acetyldibenzoylmethane changes may be considered as involving a transfer of electrons from carbon to nitrogen.

(20) The rearrangement of the quinonehydrazones



takes place with an increase in the repulsion energy of the kernels. Although the shift appears to involve complicated electron rearrangements, the evidence regarding the electron structures of benzene and quinone does not permit a complete interpretation.

The keto–enol tautomerism of the acetoacetic acid esters seems at first sight to be a case of increasing repulsion energies, since a hydrogen may shift from carbon to oxygen, O=C—C—H to H—O—C=C. However, the sum of the repulsion energies, including the double bonds, as calculated from Table I, for the two forms gives only a small positive value and at ordinary temperatures the equilibrium favors the ketone as predicted. Moreover, the rearrangement must involve some redistribution of electrons in the formation of the double bond between the carbons.

Conclusions and Summary

The results of this detailed study of the various types of organic rearrangements show: (1) the great majority of these changes take place with a decrease in the inter-kernel repulsion energy. (2) A few occur with no change in repulsion energy. These often result from a state of high activation of the molecule and the product is a mixture of the two forms. (3) Rearrangements with an increase in repulsion energy are rare

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[6] Porter, ref. 2, p. 16.

and invariably accompanied by complex redistributions of electrons in the molecule.

These observations are entirely in accord with the following premise: *if there are a number of possible arrangements of the atoms in a molecule which have the same number of electrons per atom and which satisfy equally well the tendencies of the more electronegative elements to complete their octets of electrons, that form will be the most stable which gives a minimum of repulsion between the atomic kernels.*[7]

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THE MECHANISM OF HOMOGENEOUS GAS REACTIONS. II. THE ABSORPTION SPECTRUM OF NITROGEN PENTOXIDE AND ITS METHOD OF DECOMPOSITION

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The thermal and photochemical dissociation of nitrogen pentoxide has been the subject of a number of important investigations during the past few years. Daniels and Johnston[1] showed that the thermal dissociation followed a unimolecular law and that the temperature coefficient of the velocity constant gave a mean value for the energy of activation calculated from the Arrhenius equation of 24.7 kg. cal. The average deviation of this quantity is 0.42 kg. cal. They illuminated their nitrogen pentoxide with infra-red radiation of approximately $\lambda = 1.16\mu$, corresponding to the energy values of the heat of activation, but found that there was no increased reaction due to illumination. Later investigations[2] have provided ample confirmation that neither this nor any other wave length in the infra-red causes appreciable decomposition of nitrogen pentoxide. Daniels and Johnston illuminated nitrogen pentoxide and a mixture of nitrogen pentoxide and nitrogen peroxide contained in a glass vessel by direct sunlight and found that nitrogen pentoxide decomposes only in presence of nitrogen peroxide. They isolated the region from 4000 to 4600 Å. (blue light) by filters and found that these were active wave lengths. By interposing a filter of nitrogen peroxide they showed that decomposition did not take place. Fazel and Karrer[3] proposed that the effect was due to the absorption of light by the nitrogen peroxide molecule, which then transferred its energy by a collision of the second kind to the nitrogen pentoxide molecules.

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[7] These observations are also in accord with the conclusion of Pauling and Hendricks (ref. 1) regarding the stability of certain inorganic isomers.

[1] Daniels and Johnston, THIS JOURNAL, **43**, 53, 72 (1921).

[2] Daniels, *ibid.*, **48**, 607 (1926); Taylor, *ibid.*, **48**, 577 (1926); Mayer, *ibid.*, **49**, 3033 (1927).

[3] Fazel and Karrer, *ibid.*, **48**, 2837 (1926).