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Non-adiabatic Reactions. Rotation about the Double Bond*

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I. Introduction

The experimental results of the *cis–trans* isomerization reactions which involve rotation about ethylenic double bonds show that these reactions are divided quite well into two classes.[1] They are both first order reactions, and have rate constants approximately 10^4 exp. $-25{,}000/kT$ and 10^{11} exp. $-45{,}000/kT$, respectively. It is obvious that there are at least two distinct mechanisms involved.

First order reactions "normally" have frequency factors[2] of $\sim 10^{13}$. The isomerization reaction having 10^4 for this factor is most likely non-adiabatic, *i. e.*, it must change from one potential to another with which the first interacts only in second or higher approximation. The second reaction is slower than "normal" (frequency factor 10^{11} instead of 10^{13}) for other reasons, since it is most likely adiabatic.

We shall first examine the electronic states of the double bond in an attempt to determine the potential surfaces on which these reactions take place. Then we shall consider the rates of the reactions.

II. The Double Bond Molecular Orbitals

The carbon to carbon double bond has been considered by Hückel[3] and Mulliken.[4] We shall use the molecular orbital treatment of these authors. Consider at first ethylene in its equilibrium configuration (Fig. 1). The appropriate localized molecular orbitals for the carbon atoms are

$$\left.\begin{aligned}\psi_1 &= \frac{1}{\sqrt{3}}(2s) + \frac{\sqrt{2}}{\sqrt{3}}P_z\\ \psi_2 &= \frac{1}{\sqrt{3}}(2s) - \frac{1}{\sqrt{6}}P_z + \frac{1}{\sqrt{2}}P_y\\ \psi_3 &= \frac{1}{\sqrt{3}}(2s) - \frac{1}{\sqrt{6}}P_z - \frac{1}{\sqrt{2}}P_y\\ \psi_4 &= P_x\end{aligned}\right\} \qquad (1)$$

$(2s)$ is the s orbital of principal quantum number 2; P_x, P_y and P_z are the real $2p$ orbitals directed along the x, y, and z axes, respectively, ψ_1, ψ_2 and ψ_3 are equivalent bonds directed at 120° angles. We shall use subscripts to designate the carbon atom to which they belong. $\psi_{1a} + \psi_{1b}$ forms the so-called σ part of the double bond; $\psi_{4a} + \psi_{4b}$ forms the π part. ψ_{2a} and ψ_{3a} form bonds with the hydrogen atoms α and β, respectively; ψ_{2b} and ψ_{3b} bind the other hydrogen atoms.

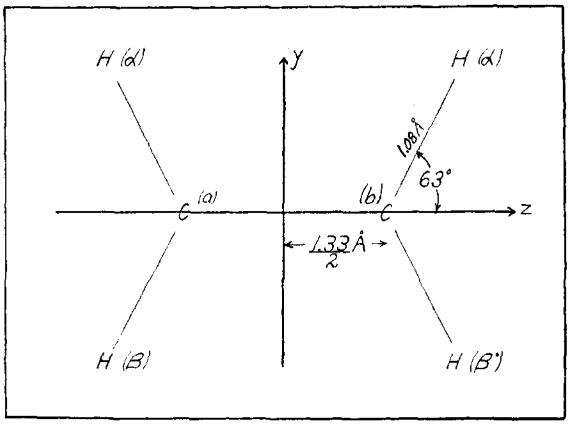

Fig. 1.—The ethylene molecule in the coördinate axes used in this paper. The dimensions assumed are also given.

As usual we shall assume that the state of the molecule can be represented sufficiently well by the two electrons forming the π bond. Thus we write for the ground state of the ethylene molecule

$$\psi_{\text{I}} = \frac{1}{2}\{P_{xa}(1) + P_{xb}(1)\}\{P_{xa}(2) + P_{xb}(2)\}\,\frac{(\alpha_1\beta_2 - \alpha_2\beta_1)}{\sqrt{2}} \qquad (2)$$

α_1 indicates a positive z component of the spin of electron 1, β_1, a negative z component for the spin of 1.

Another singlet state is

$$\psi_{\text{II}} = \frac{1}{2}\{P_{xa}(1) - P_{xb}(1)\}\{P_{xa}(2) - P_{xb}(2)\}\,\frac{(\alpha_1\beta_2 - \alpha_2\beta_1)}{\sqrt{2}} \qquad (3)$$

Both electrons have been promoted to the anti-bonding orbitals, and so the state has considerable excitation energy. However, it is to be noted that on rotation of one of the CH_2 groups by 180° (the rotation which takes *cis* to *trans* in substituted ethylenes) the bonding and anti-bonding

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* Paper presented at the Symposium on the Transfer of Energy in Molecular Collisions, American Chemical Society Meeting, Detroit, Michigan, September, 1940.

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[1] Experimental papers on *cis–trans* isomerization: (a) I, Kistiakowsky and Nelles, *Z. physik. Chem.*, **152**, 369 (1931); II, Nelles and Kistiakowsky, THIS JOURNAL, **54**, 2208 (1932); III, Kistiakowsky and Smith, *ibid.*, **56**, 638 (1934); IV, **57**, 269 (1935); V, **58**, 766 (1936); VI, **58**, 2428 (1936). (b) I, Tamamusi and Akujama, *Z. Elektrochem.*, **43**, 156 (1937); II, *Bull. Chem. Soc. Japan*, **12**, 382 (1937); III, *Z. Elektrochem.*, **45**, 72 (1939). (c) Hojendahl, *J. Phys. Chem.*, **28**, 758 (1924). (d) Ebert and Bull, *Z. physik. Chem.*, **152**, 451 (1931). (e) Hartley, *J. Chem. Soc.*, 633 (1938).

[2] A reaction rate constant can be written as $Ae^{-E_a/kT}$. A is the frequency factor and E_a the activation energy.

[3] Hückel, *Z. Physik*, **60**, 423 (1930).

[4] Mulliken, *Phys. Rev.*, **41**, 751 (1932).

orbitals change their rôles, and ψ_{II} becomes the ground state of the molecule. If the molecule rotates in such a way as to remain in the original singlet state during the entire process there will be strong resonance between ψ_{I} and ψ_{II}, especially in the vicinity of the 90° angle, and the electrons will change from one state to the other.

The lowest excited state of the ethylene molecule is a triplet state.[4,5]

$$\psi_{\mathrm{III}} = \frac{1}{2\sqrt{2}}\{(P_{\mathrm{xa}}(1) + P_{\mathrm{xb}}(1))(P_{\mathrm{xa}}(2) - P_{\mathrm{xb}}(2)) - (P_{\mathrm{xa}}(2) + P_{\mathrm{xb}}(2))(P_{\mathrm{xa}}(1) - P_{\mathrm{xb}}(1))\}\, S_{\mathrm{III}} \quad (4)$$

Here S_{III} designates the spin function and can be $\alpha_1\alpha_2$, $(\alpha_1\beta_2 + \alpha_2\beta_1)/\sqrt{2}$ or $\beta_1\beta_2$.

A schematic diagram showing the behavior of the energies corresponding to ψ_{I}, ψ_{II} and ψ_{III} on rotation about the double bond is given in Fig. 2. No calculation of energies has been made, but it is quite certain that qualitatively these surfaces are placed correctly. The low triplet state is not surprising since ethylene is isoelectronic with the oxygen molecule. For the configuration with $\theta = 90°$ this should be the lowest state since the singlet double bond is completely destroyed, and the triplet state depends comparatively little on rotation.

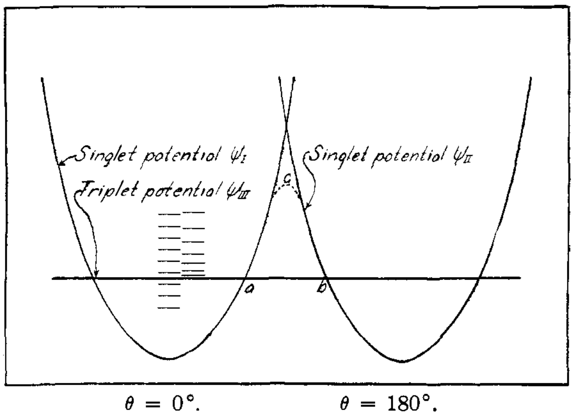

Fig. 2.—Schematic illustration of the potential assumed in this work for the rotation around the double bond in ethylenic compounds. The energy levels are not drawn to scale. The molecule could in general never change from the singlet to triplet state, if this degree of freedom were orthogonal to the other molecular motions, because the levels do not match.

III. The Two Reaction Mechanisms

The proposed mechanisms for the rotation reactions can be seen from Fig. 2. The mechanism having a high frequency factor and large activation energy involves going over the large barrier, the eigenfunction changing from ψ_{I} to ψ_{II} as the system moves along the dotted section of the reaction path. The activated state comes at c and the molecule remains in a singlet state thoughout this process. It is believed that the other mechanism involves changing to the triplet surface. The low frequency factor is a result of the difficulty associated with this change, which is made at the points a and b. The activation energy is of course smaller for this latter mechanism.

Qualitatively these potential surfaces are in agreement with the experimental observations. In order to make as much of a quantitative check as possible with the available experimental data we must approximate the potential, and we do this from the infrared spectrum of ethylene. Bonner[6] gives as the torsional frequency for ethylene 825 cm.$^{-1}$. Using the dimensions for the molecule given in Fig. 1 the force constant k is calculated to be 3.75×10^{-12} dynes per radian. The parabolic potentials having this force constant are shown in Fig. 2 as the heavy lines. The crossing point of these comes at 63,000 calories/mole above the minimum. The actual potential for the singlet state will be somewhat lower than this, as given by the dotted line. The experimentally observed activation energies for this mechanism vary from 40,000 to 48,000 calories/mole. We shall assume that this parabolic potential is the one to use. The torsional frequencies for most of the molecules in which we are interested are not known, and when necessary they will be calculated from this potential.

The triplet potential, having no angular dependence, is placed at ~ 20,000 calories/mole above the singlet minimum.

IV. Reaction with Low Activation Energy

A. Classical Treatment

First we shall assume that the energy levels for the rotational motion are continuous at the activated state and the reaction can be treated in the usual manner. In most reactions there is classical motion along the reaction path, or at least on one side of the activated state (for example, a unimolecular decomposition leads from a quantized vibrational level to a continuum of translational levels). In this particular reaction there are three potentials with well quantized

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[5] Mulliken, *J. Chem. Phys.*, **7**, 120 (1939).

[6] Bonner, This Journal, **58**, 34 (1936).

energy levels. We shall expect the classical rate to be greater than the observed rates since the quantization restricts the motion. In the next part of this section we shall consider in detail the effects to be expected from the quantization.

The activated state for this reaction occurs at either the point a or the point b. For compounds having *cis* and *trans* forms these are not equivalent and the passing at one of these points will be rate determining. We assume that it is at a. The rate constant for this reaction is

$$k_1' = \kappa_1 \frac{kT}{h} \cdot \frac{F_1^{\pm}}{F_N} e^{-E_a/kT} \qquad (5)$$

Here $F_1^{\pm}$ is the partition function for the activated state at a from which the torsional degree of freedom has been removed; F_N is the partition function for the normal molecule. We shall assume further that the activated molecule has identical properties with the normal one in every way except the torsional motion. This gives

$$k_1 = \kappa_1 \frac{kT}{h} (1 - e^{-h\nu_\theta/kT})\, e^{-E_a/kT} \qquad (6)$$

Now we must consider κ_1. Without this factor we have the equilibrium number of molecules which are in the singlet potential at the point of crossing. This must be corrected in two ways; so for convenience we shall write

$$\kappa_1 = \rho_1 \sigma_1 \qquad (7)$$

The factor ρ_1 gives the probability for the transfer to the triplet potential which is necessary for the reaction to occur. It depends upon the nature of the two potential surfaces and the magnitude of their interaction. The factor σ_1 corrects for the molecules which react and then return. $(1 - \sigma_1)$ gives the fraction of molecules at the activated state which came from the final state. This factor depends upon the ease of transferring energy from one molecule to another and thus will depend upon the pressure. The product must be deactivated, or else it will return to the initial state, since obviously it has enough energy to do this. At first we calculate the "high pressure rate," valid when $\sigma_1 = 1$.

Zener and Landau[7] find for ρ_1 the expression

$$\rho_1 = 1 - \text{exp.}\left(-\frac{4\pi^2\epsilon^2}{hv\,|S_i - S_f|}\right) = 1 - \text{exp.}\,(-a) \quad (8)$$

where ϵ is the interaction energy between the singlet and triplet states; v is the velocity of motion on the potential surfaces; $|S_i - S_f|$ is the absolute value of the difference of the slopes of the two potentials at their intersection.

The estimation of ρ_1 is carried out in Appendix I for butene-2 and maleic acid methyl ester, two examples of molecules which isomerize by this mechanism. For high pressure rates of these two reactions we calculate

$$\text{butene-2, } k_1 = 2.76 \times 10^{-7} \times 9.2 \times 10^{12}\ \text{exp.}\,(-E_a/kT) = 2.54 \times 10^{5}\ \text{exp.}\,(-E_a/kT)$$

$$\text{maleic ester, } k_1 = 1.22 \times 10^{-7} \times 3 \times 10^{12}\ \text{exp.}\,(-E_a/kT) = 3.66 \times 10^{5}\ \text{exp.}\,(-E_a/kT)$$

The observed high pressure rate for maleic ester[1aII] is 1.3×10^5 exp. $(-26.5/kT)$ but that for butene-2[1aV] is considerably lower. It is given as 10° exp. $(-18.0/kT)$. If the activation energy is in error by enough to make it the same as that for maleic ester, the frequency factor is only $\sim 10^2$. According to the theory presented here the reason for the low rate for butene-2 is classified as "quantum effects" due to the wide spacing of the energy levels for motion along the reaction path. The levels of maleic ester are closer together and thus it more nearly meets the classical requirement of the above calculation.

Now let us consider the factor σ_1. A molecule after passing the activated state has a number of possibilities. The ratio of the rates at which it becomes deactivated to the sum total of the possible reactions (including the ways of returning to the initial state) gives the factor σ_1. The rate of returning to the initial state is just $\rho_1 A_1$ since the activation energy is already in the molecule. A second possibility is the deactivation in a collision; the rate of this is $\alpha_c \nu_c$ where ν_c is the frequency of collision and α_c is the probability for the deactivation. Other possibilities are the transfer of the energy to other degrees of freedom, or "internal collisions"; these have rates $\alpha_i \nu_i$ where ν_i is the frequency with which the possibility occurs for transferring energy to the i^{th} vibration and α_i is the probability. These last reactions are not certain to deactivate the molecule since the energy is still there and will return to the same degree of freedom after a time τ_i for the i^{th} vibration. Thus the probability for deactivation if the energy is transferred to another degree of freedom is

$$\alpha_i \nu_i \frac{\alpha_c \nu_c}{(1/\tau_i) + \alpha_c \nu_c}$$

since ultimately collisions must remove the excess energy. There is no dipole moment for the torsional motion, and so the energy cannot

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[7] (a) Zener, *Proc. Roy. Soc.* (London), **A140**, 660 (1932); (b) Landau, *Physik. Z. Sowjetunion*, **2**, 46 (1932).

be radiated very easily. Putting the above discussion into equation form, we get

$$\sigma_1 = \frac{\alpha_c\nu_o + \sum_{i=1}^{m} \alpha_i\nu_i \frac{\alpha_o\nu_c}{1/\tau_i + \alpha_o\nu_o}}{\rho_1 A_1 + \alpha_c\nu_o + \sum_{i=1}^{m} \alpha_i\nu_i} \qquad (9)$$

There are m vibrations into which the energy can go.

Experimentally the isomerization reactions discussed above (butene-2 and maleic ester) are pressure dependent at $\sim$ 1 atmosphere. If we assume that all $\alpha_i\nu_i$ are zero, 9 becomes

$$\sigma_1 = \frac{\alpha_o\nu_o}{10^5 + \alpha_o\nu_o} \cong \frac{\alpha_c 10^9}{10^5 + \alpha_o 10^9} \qquad (10)$$

Thus it is seen that for σ_1 to be pressure dependent at one atmosphere α_c must be $\sim 10^{-4}$. Collisions must be very inefficient in transferring energy from the torsional motion of these molecules, even though they are in fairly high vibrational states. If the $\alpha_i\nu_i$ are different from unity, α_c must be reduced still further. Thus we are forced to the conclusion that the transfer of energy to and from the torsional degree of freedom is difficult. This conclusion is valid even when quantum effects are considered.

The pressure dependence which Kistiakowsky and Nelles[1aII] report for maleic ester is of the form of 12 and gives further support to the correctness of the interpretation. They give

$$\sigma_1 = 1\Big/\left(1 + \frac{1400}{p}\right)$$

where p is the pressure in millimeters. Comparing this with equation 10 we get

$$\frac{10^5}{\alpha_o \times 10^9} = \frac{1400}{760},\ \alpha_o = 5 \times 10^{-5}$$

Giving α_c this value makes the calculated rate of the *cis–trans* isomerization reaction for maleic acid dimethyl ester in good agreement with experiment. The agreement for butene-2 is poor, and now we shall consider the quantum treatment which should also explain this.

B. Quantum Treatment

In Fig. 2 the placing of the energy levels in the initial singlet and the triplet levels are indicated in schematic fashion. These are the hypothetical levels which would be the correct ones for the molecule if the torsional motion were not coupled with the other vibrations of the molecule, or with the rotation of the molecule as a whole. In general none of these levels can be expected to match exactly in the two levels. Since conservation of energy makes impossible radiationless transitions between energy levels which are not "in resonance," one should not expect a reaction at all for the system of Fig. 2. There are, however, a number of ways by which the energy levels can be made to match.

A first method would be a direct interaction with a translational degree of freedom. During a collision the translational continuum could make the energy levels match quite well. However, this process would be bimolecular, and the experimental results of the *cis–trans* reactions indicate that they are first order for sufficiently high pressures. Apparently there are other reactions which take place more rapidly than this process, and so we shall not discuss it further.

The levels of Fig. 2 will be split many times and displaced when the coupling with the other motions of the molecule are considered. This smearing out of the levels may be sufficient to permit the transition.

A third way for the transition to take place is for another transition to take place simultaneously, *i. e.*, resonance between energy levels for the total molecule, as contrasted with energy levels for one degree of freedom only as we have been considering. This would necessitate a fairly strong coupling between the rotary motion and other degrees of freedom.

In quantum mechanics degeneracy does not mean that two levels coincide to an infinitesimal degree but that their energy difference is smaller than the energy matrix element which joins them. It is shown in Appendix I that the interaction between the singlet and triplet electronic states is less than a small calorie. This interaction is not the complete matrix element, since an overlap of the vibrational function in the singlet with the rotation of the triplet enters also and this is a small number. The energy levels must, therefore, be quite well matched for the necessary degeneracy. We shall assume for the present that this condition can be satisfied and proceed to calculate the rate of reaction.

If we consider only the torsional vibration, the wave function for the initial state of the molecule is written as a product of an electronic and a vibrational part.

$$\Phi_{\mathrm{In}} = \psi_1\theta_{\mathrm{In}} \qquad (11)$$

θ_{In} is the vibrational wave function for the n^{th} level of the singlet parabolic potential.

If this level is matched by the m^{th} level in the triplet state the final wave function is

$$\Phi_{\text{fm}} = \psi_{\text{III}}\theta_{\text{IIIm}} \tag{12}$$

The wave function for the molecule will oscillate between these two with a frequency which can be determined by means of the time dependent perturbation theory. The state of the molecule is

$$\Psi_{\text{nm}} = \{c_{\text{i}}\Phi_{\text{in}} + c_{\text{f}}\Phi_{\text{fm}}\}\, e^{2\pi i E_{\text{nm}}t/h} \tag{13}$$

The c's are time dependent. It can be shown that the probability for the final state changes with time as

$$C_{\text{f}}^{*}C_{\text{f}} = \sin^2 \frac{2\pi H'_{\text{if}}}{h}\, t \tag{14}$$

and the molecule oscillates from the initial to the final state with a frequency H'_{if}/h. Thus we can write the rate with which the reaction takes place when the molecule is in the n^{th} singlet vibrational state, in the usual manner, as a ratio of partition functions times this frequency factor.

$$k'_{\text{1n}} = \kappa_{\text{1n}} \left(\frac{H'_{\text{if}}}{h}\right)_{\text{n}} \frac{\dfrac{(2\pi mkT)^{3/2}}{h^3} \sum 4(j + {}^1/_2)\gamma_{\text{nj}}\, e^{-\frac{(j + {}^1/_2)^2h^2}{8\pi^2(ABC)^{1/2}kT}} \sum\limits_{\substack{i=1\\k=0}}^{\substack{\infty\\ \text{f}}} \gamma_{\text{ik}}\, e^{-\frac{(k + {}^1/_2)h\nu_{\text{i}}}{kT}}\, e^{-\frac{(n + {}^1/_2)h\nu_\theta}{kT}}}{\dfrac{(2\pi mkT)^{3/2}}{h^3}\, \dfrac{8\pi^2(8\pi^3ABC)^{1/2}(kT)^{3/2}}{h^2} \prod\limits_{i=1}^{\text{f}} \left(1 - e^{-\frac{h\nu_{\text{i}}}{kT}}\right)^{-1} \sum\limits_{l=0}^{\infty} e^{-\frac{(l + {}^1/_2)h\nu_\theta}{kT}}} \tag{15}$$

κ_{1n} is the usual over-all correction factor. H'_{if} depends somewhat on n and so we introduce this subscript to indicate the level. The reaction can take place only for certain of the rotational and vibrational states, since it is difficult to match the initial and final levels properly; γ_{nj} gives the fraction of the $4(j + {}^1/_2)$ rotation states which can lead to a reaction. Similarly γ_{ik} indicates whether the n and m levels are matched when there are k quanta of excitation energy in the i^{th} vibrational degree. Since we cannot calculate these many factors a few simplifications will be made.

$$k'_{\text{1n}} = \kappa_{\text{1n}} \frac{(H'_{\text{if}})_{\text{n}}}{h} \gamma_{\text{n}}\, e^{-(n + {}^1/_2)h\nu_\theta/kT} \left(\Sigma\, e^{-(l + {}^1/_2)h\nu_\theta/kT}\right)^{-1} \tag{16}$$

γ_{n} is the proper average of the $\gamma_{\alpha\beta}$ which gives the fraction of the time the n and m^{th} levels are matched so that the reaction can take place. Now we proceed to sum over all levels. Since the torsional vibration has a quantum of energy usually smaller than kT, integration is substituted for the summation. Also averages are taken for $(H'_{\text{if}})_{\text{n}}$ and κ_{1n}.

$$k'_1 = \kappa_1 \frac{H'_{\text{if}}}{h} \gamma \frac{\int_n^\infty e^{-(l + {}^1/_2)\epsilon_0/kT}\, \mathrm{d}l}{\int_0^\infty e^{-(l + {}^1/_2)\epsilon_0/kT}\, \mathrm{d}l} = \kappa_1 \frac{H'_{\text{if}}}{h} \gamma\, e^{-(n + {}^1/_2)\epsilon_0/kT} \tag{17}$$

where ϵ_0 is $h\nu_0$.

Now let us consider the matching of the energy levels. It is shown in Appendix II that $H'_{\text{if}} \sim 1.5 \times 10^{-2}$ calories/mole for maleic ester. The energy levels must have a separation of this order of magnitude or less. If we take (as in Appendix II) a reduced moment of inertia for the internal rotation of maleic ester 53×10^{-39} g. sq. cm.[2] we get $h^2/4\pi^2I = 0.29$ calorie. The spacing of the levels in the singlet vibration is 125 calories. For this distance above the triplet potential there are 29 rotational levels. Thus the average separation is $\sim 4 \cong \frac{125}{29}$ calories in this vicinity, which is much too coarse compared with 10^{-2}. However, these levels are split and displaced considerably by the other motions of the molecule. An internal rotation couples especially strongly with the rotation of the molecule as a whole.[8] Taking the moments of inertia for the molecule as 50×10^{-39} we calculate from the partition function $8\pi^2(8\pi^3ABC)^{1/2}(kT)^{3/2}/h^3$ that there are 10^6 rotational states. Thus there is reason to expect enough overlapping of levels, in fact the average separation instead of being $\sim$ 4 calories may well be $\sim 4 \times 10^{-6}$.[9]

In this connection it is well to note that these considerations do not depend very greatly upon the details of the model proposed. It is certain, for example, that maleic ester cannot actually have completely free rotation on the triplet level, since steric hindrance can prevent it for certain configurations. This motion will be re-

(8) See, for example, Koehler and Dennison, *Phys. Rev.*, **57**, 1006 (1940).

(9) If the levels are spaced this closely then there are many ($10^{-2}/10^{-6} = 10^4$ levels) which may react with each initial singlet level. One might be inclined to treat the problem as a transition from a quantized level to a continuum, in which case a different result would be obtained from that given above. However, it is to be noted that for a given molecule there is only access to *one* of these many levels at a time, and thus the treatment given above is correct.

duced to a torsional motion of some sort, having a small force constant. But there will be certain vibrations which are appreciably affected by molecular rotations and these will be excited sufficiently to cause the splitting described above.

Now we shall attempt to estimate γ. If we assume that the molecular motions smear the triplet levels uniformly, then the fraction of states which can be utilized by the molecule in going from the singlet to the triplet is the ratio of the width of a line[10] to their separation in the singlet state. Thus for maleic ester $\gamma \sim 1{,}5 \times 10^{-2}/125 = 1.2 \times 10^{-4}$ and for the high pressure rate of reaction we calculate

$$\begin{aligned} k_1' &= 1.5 \times 10^{-2} \times 1.056 \times 10^{10} \times 1.2 \times 10^{-4} \times e^{-E_a/kT} \\ &= 1.9 \times 10^{4}\, e^{-E_a/kT} \end{aligned}$$

This rate is smaller than the observed rate by a factor of ten, but due to the roughness of the approximations it is in quite satisfactory agreement.

For butene-2 the levels are spaced much more widely apart and so γ is smaller. Calculated as above for maleic ester we obtain $\gamma \sim 10^{-5}$ and this gives a rate

$$\begin{aligned} k_1' &= 2.5 \times 10^{-2} \times 1.056 \times 10^{10} \times 10^{-5}\, e^{-E_a/kT} \\ &= 2.7 \times 10^{3}\, e^{-E_a/kT} \end{aligned}$$

and this is a larger frequency factor than is observed. We have said that the principal cause of the smearing of the triplet states is the rotation of the molecule as a whole. Butene-2 has fewer rotational states than maleic ester, and thus one should expect less success in shifting the levels sufficiently. If we make a calculation parallel to that for maleic ester for the average separation of the levels in the triplet potential we obtain ~ 0.02 calorie (to be compared with 4×10^{-6} for maleic acid). This is the order of magnitude of H'_{if}, and so the reaction is expected to take place. But we may well expect the rate to be slower than that for maleic ester by a factor $4 \times 10^{-6}/2 \times 10^{-2} = 2 \times 10^{-4}$. The experimentally observed ratio of the rates of these reactions is 10^{-3}. There seems to be a proportionality between γ and the number of rotational states as one might expect from the above discussion.

C. Reaction Rate Expression for κ

The expression for κ given in equation 11 is essentially correct even in the quantum formulation. We shall discuss the rates of the various reactions which appear in κ from the point of view used in part B of this section. First let us consider the rate at which a molecule in a particular vibrational state loses energy to other vibrations. We observe that this is exactly the problem discussed in part B—a molecule in one state changes to another with which it is in resonance; so by a development parallel to that by which equation 11 was obtained, we write

$$k_i' = \alpha_i \nu_i = \frac{H'_{\mathrm{ni}}}{h}\, \gamma_{\mathrm{ni}}\, e^{-(n + 1/2)h\nu_\theta/kT}(1 - e^{-h\nu_\theta/kT}) \tag{18}$$

If we are just considering the molecules which are actually in this particular state we include the exponential terms in the concentration and

$$\alpha_i \nu_i = \frac{H'_{\mathrm{ni}}}{h}\, \gamma_{\mathrm{ni}} \tag{19}$$

H'_{ni}/h is identified with the frequency ν_i. The actual form of this frequency factor may be somewhat different from a matrix element divided by h depending upon the particular case. However, it will always be essentially this; α_i is identified with γ_{ni}. There is no κ factor in this rate constant because we have explicitly written κ in equation 11. It is clear that the molecule will not remain in the i^{th} state and the energy must ultimately be lost in a collision.

$1/\tau_i$ may be just equal to $\alpha_i \nu_i$ or it may be the sum of a number of reaction rate constants depending upon how well the i^{th} vibrational state is connected with other vibrational states.

Now let us consider the number of states (m of equation 11) that there are for this vibration to interact with. There are $(x - y - 1)!/x!\,(y - 1)!$ ways to distribute x quanta of vibrational excitation among y oscillators. There are 12 double bond vibrations and their average quantum should be $\sim$ 3 or 4 kcal. Thus for 20 kcal. of excitation (which corresponds to the final state for the isomerization reactions being considered) there are about 6 quanta and thus about 12,000 states. The average difference for these quanta will be on the order of one hundred calories and so the average separation at 20 kcal. excitation will be $100/1200 \sim 0.01$ calorie. As we have noted earlier the number of states with which one particular state can resonate depends upon the magnitude of the matrix element connecting the states. In all probability two of these states which are adjacent differ quite radically in the distribution of the excitation and thus have very

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(10) For this we take the magnitude of the matrix element which connects it to other levels.

small interaction. The largest matrix elements are between states which only differ in one or two quanta between the initial and final states. The probability for finding two strongly interacting states at fairly low excitation with the same energy is in general quite small, most likely there is practically no interaction of this state with others near in energy and m is zero. The probability for an "internal collision" should be small in this particular case.

In this paper we are primarily interested in "internal collisions" rather than collisions with other molecules, and we shall leave the rate of transfer of vibrational energy in collision as $\alpha_c\nu_c$. There is, however, another pressure effect which the quantum treatment introduces and which will be discussed at this time.

In the above discussion in part B of this section of the density of levels we have tacitly assumed that the molecular levels are infinitesimal in width. If they depend upon radiation for changes for all practical purposes this is true, because the mean lives of oscillators and rotators are quite long. By the uncertainty principle we have $\tau\delta E \sim h/2\pi \sim 10^{-11}$ calories seconds.

$$\delta E = \frac{10^{-11}}{\tau} \text{ calories} \qquad (20)$$

An oscillator has a mean life $\sim$ 0.1 second and thus a line width of $\sim 10^{-10}$ calorie.

The rearrangement of levels in our reaction mixtures comes not by radiation but by collisions. If a particular level has a life $\tau = 1/\alpha_c\nu_c$ where α_c is the frequency of collisions and ν_c is the probability for a change at each collision, the breadth of the level will be

$$\delta E = 10^{-11}\, \alpha_0\nu_c \text{ calories}$$

Since collision frequencies are of the order of 10^9 for atmospheric pressure a level which changes frequently may have a breadth $\sim 10^{-2}$ calories. In case the matrix element H'_{if} is smaller than this, a considerable pressure effect may result from this cause.

In the two cases under consideration in this section, butene-2 and maleic ester, this effect is probably not so important. The principal pressure effect is most likely that described in part A of this section.

V. Reaction with High Activation Energy

If it is assumed that the activated state is at the point c of Fig. 2, the formulation of the reaction rate constant is parallel to that of part A, Section IV.

$$k_2' = \kappa_2 \frac{kT}{h} (1 - e^{-h\nu_\theta/kT})\, e^{-E_a/kT} \qquad (21)$$

Using the parabolic potential discussed previously and rough moments of inertia to calculate ν_θ, the calculated rate constants for three reactions reported by Kistiakowsky and Smith[1a] are given in Table I.

TABLE I

Compound	Calcd.	Calcd. rate	Observed rate
Stilbene	50 cm.$^{-1}$	$1.4 \times 10^{12}\, e^{-E_a/kT}$	$6.0 \times 10^{12}\, e^{-42.8/kT}$
β - Cyano - styrene	92	$2.0 \times 10^{12}\, e^{-E_a/kT}$	$4.0 \times 10^{11}\, e^{-46.0/kT}$
Methyl cinnamate	63	$1.7 \times 10^{12}\, e^{-E_a/kT}$	$3.5 \times 10^{10}\, e^{-41.6/kT}$

The frequency factors for the first two are approximately off by factors of five, but the third is low by a factor of fifty. This does not take into account the factor κ, and this can probably account for the discrepancy.

The κ factor given in equation (11) is used to correct the rate expression 28. This factor does not necessarily bring in a pressure dependence (experimentally these reactions have no pressure dependence). For appropriate values of the $\alpha_i\nu_i$ there can be a large decrease in the rate of a unimolecular reaction with no pressure effect. The slow process is actually the transfer of energy to other vibrational degrees of freedom, after the rotation has taken place. The formulation as we have carried it out above is still correct. First the equilibrium concentration of a certain kind of molecule is calculated—the molecules which can perform the reaction in question. Then all possibilities of reaction for these are considered and separated into two groups: some of them lead successfully to the particular reaction of interest and some of them do not. The κ factor of equation (11) gives the correct rate.

There are two factors which make one expect larger values of the $\alpha_i\nu$ for this mechanism than the previous one. In the first place the density of levels is much greater. One estimates that there are $\sim 10^8$ levels having 45 kcal. excitation as compared with 12,000 for 20 kcal. A more important factor is the nature of the interactions among the vibrations. For a plane configuration of the molecule the torsional motion is a normal vibration.[11] Due to the highly symmetrical

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(11) Bonner (ref. 6) has classified the vibrations for the case of ethylene. The other considerations in this section are by standard group theory methods such as discussed by Rosenthal and Murphy, *Rev. Mod. Phys.*, **8**, 317 (1936).

nature of the potential this should still be a good approximation when the excitation is 20 kcal./mole. For the molecule which is rotated at an angle $\theta = 90°$ the situation is different. The torsion is no longer a normal vibration, but interacts with eight of the other eleven double bond vibrations. Thus when there is enough excitation in this vibration so that the molecule can actually rotate, there is strong interaction with other vibrations which are very nearly orthogonal when the molecule is near its normal state.

Unfortunately the actual estimation of such quantities as the α_i and ν_i is difficult. In fact it is impossible at present to predict the order to be expected for the three reactions of Table I.

VI. Discussion of Experimental Results

In Table II are assembled the available experimental results of the *cis–trans* isomerizations. It is seen that they actually fall quite well into one or the other of our two classes. Up to this time we have said nothing as to which class a given compound should belong. We shall discuss that now.

The triplet level is principally concerned with the double bond orbitals and, being of different multiplicity, does not interact very strongly with other low electronic states of the molecules. Consequently it is expected that this level should be at nearly the same height in all of these molecules, including, of course, the ones which go by the higher route. The singlet level on the other hand, should differ quite greatly from one molecule to another in the region of the activated state. This is because one of the double bonds is completely broken, and the energy of the molecule now depends upon the ability of these two electrons, which can no longer form a π bond, to furnish some other kind of binding. In molecules with phenyl groups attached to the double bond, for example, there is ample opportunity for resonance. In a molecule such as butene, or even maleic acid, there is very little that these electrons can do.

It is to be noted that the molecules which have an opportunity for resonance go by the higher route, *i. e.*, stilbene, chlorostilbene, etc.

One should expect on the basis of this discussion that the reactions with the higher activation energy should be faster than those with the lower activation energy. This seems to be the case. Conceivably there may be exceptions due to specific quantum effects, but this seems unlikely.

Two values are reported for maleic acid dimethyl ester (see Table II). We have given preference to that reported by Kistiakowsky and Smith,[1aV] $1.3 \times 10^5 e^{-26.5/kT}$. It is well to notice that the absolute rates of these two are not far different, although the activation energies differ considerably. The authors reporting the second value, Tamamusi and Akujama,[1b] have done some interesting work on the effect of paramagnetic substances on this particular isomerization reaction. The fact that paramagnetic catalysts accelerate the reaction gives support to the mechanism involving the triplet state. The report is, however, that the activation energy as well as the frequency factor is changed and this is hard to reconcile with the model as presented here.

The azo compounds[1e] are isoelectronic with the ethylenic compounds and one expects a similar potential for the rotation. There seems to be no

TABLE II

Compound	T, °C.	$p_{\text{mm.}}$	Frequency factor	E_a (kcal.)	ΔH isomerization
Maleic acid (liq)	140–150	....	1.67×10^4	15.8	
Maleic acid di-Me ester (g)	270–380	45–530	1.3×10^5	26.5	−6200 (s)
Maleic acid di-Me ester (g)	270–320	15–90	3.2×10^3	17.7	−6000 (g)
Di-Me citraconate (g)	280–360	30–500	10^5	25.0	−3100 (s)
Butene-2 (g)	390–420	100–1440	2 (?)	18.0	− 950
Me cinnamate (g)	290–387	5–500	3.5×10^{10}	41.6	−6000 (g)
β-Cyanostyrene	308–378	20–450	4×10^{11}	46.0	Small
Stilbene (g)	280–338	4–400	6×10^{12}	42.8	−3000
Stilbene (1)	214–223	....	2.7×10^{10}	36.7	
Mono-Cl-stilbene (1)	226–246	....	1.4×10^{11}	37.0	
Di-Cl-stilbene (1)	175–196	....	9.9×10^{10}	34.1	
4-Cl, 4-Br, 4-NO_2 Diazobenzene cyanide (benzene soln.)	25–57.5	....	5×10^{10}–10^{11}	21.6–22	
Azobenzenes (various solvents)	19–100	....	10^{10}–10^{11}	23.0	−12000 (21°)

evidence for a non-adiabatic process. The reaction in which the molecule stays singlet goes with such a low activation energy (~ 25 kcal.) that there is probably never an advantage for the triplet state.

The mechanism of this isomerization is not known. There is an additional possibility due to the fact that the nitrogen atom has only two groups attached. The molecule can change from *cis* to *trans* retaining a plane structure throughout the process. However, it seems that the activated state should consist of the molecule in which the double bond is broken, and about the same activation energy is expected for both possibilities.

VII. Tunneling in Rotation Around Double Bonds

Since the existence of the triplet level which we have suggested here has not been verified, it seemed to be necessary to investigate the possibility that tunneling could be the explanation for the mechanism with low activation energy. In certain cases it is known that there is a leakage through potential barriers. For example NH_3 penetrates a narrow barrier 10^{10} times per second in an inversion type reaction. Studies of the ammonia problem have been made by a number of investigators.[12] They have shown that the results are not very sensitive to the exact form of potential used. Thus we can expect order of magnitude accuracy for the rate of the tunneling reaction with the potential described earlier in this paper. In Fig. 3 this potential is shown again with the notations to be used in this section.

Following the treatment of Dennison and Uhlenbeck[12b] for ammonia, we first join the two parabolas with the straight line $a - b$ (Fig. 3) to give a barrier of height 50 kcal. These authors have developed an analytical expression for the splitting of the energy levels due to the coupling of the motion in the two minima when this type of potential is used. The magnitude of the splitting is a measure of the rate at which the system goes from one minimum to the other. The splitting for the n^{th} level depends upon the area enclosed by the lines $\overline{ab}$ and $\overline{\theta_1\theta_2}$ with the parabolic sections. Because the area is the important factor rather than the exact shape of the potential, it is easy to obtain order of magnitude accuracy.

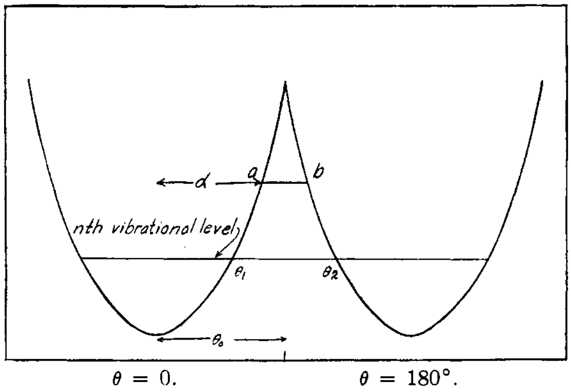

Fig. 3.—Potential used to discuss the tunneling reaction of ethylenic compounds.

As we have seen earlier it is necessary to have exact degeneracy for such a process to occur at all, and it will be more difficult in this case than in the one discussed. We shall assume that this condition is satisfied and proceed with the calculation.

In a manner entirely analogous to that of Section IV we find that the rate at which the tunneling reaction proceeds when the vibrator is in the n^{th} level is

$$k'_n = \frac{\Delta_n}{h} e^{-(n + 1/2)h\nu_0/kT} (1 - e^{-h\nu_0/kT}) \qquad (22)$$

Δ_n/h is the frequency factor H'_{if}/h.

For the parabolic potential described above the analytical expression of Dennison and Uhlenbeck of Δ_n is

$$\frac{\Delta_n}{h} = \left(\frac{1}{\pi}\right) \left[\frac{\alpha + (\alpha^2 - 2n - 1)^{1/2}}{(2n + 1)^{1/2}}\right]^{2n + 1} \exp\left[-(2\theta_0 - \alpha)(\alpha^2 - 2n - 1)^{1/2}\right] \qquad (23)$$

where

$$\alpha = \left[\frac{4\pi^2 I_r \nu_0}{h}\right]^{1/2} \theta_a \qquad \theta_0 = \left[\frac{4\pi^2 I_r \nu_0}{h}\right]^{1/2} \frac{\pi}{2}$$

I_r is the reduced moment of inertia for the vibration, ν_0 is the frequency of vibration.

For ethylene we get the rate of the tunneling reaction in the tenth level

$$k'_{10} = 7.2 \times 10^3\, e^{-23,000/kT} \qquad (24)$$

and in the twentieth level

$$k'_{20} = 5.2 \times 10^{11}\, e^{-46,000/kT} \qquad (25)$$

For ethylene it appears that the rate of the tunneling is of the right order of magnitude to be of importance in isomerization reactions. In order to see how sensitive this result is to the potential barrier we place the line $\overline{ab}$ lower by 5 kcal., making it at 45 kcal. The rate for the tenth level is now increased by a factor of ten,

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[12] (a) Morse and Stueckelburg, *Helv. Phys. Acta*, **4**, 337 (1931); (b) Dennison and Uhlenbeck, *Phys. Rev.*, **41**, 313 (1931); (c) Rosen and Morse, *ibid.*, **42**, 210 (1932); (d) Manning, *J. Chem. Phys.*, **3**, 136 (1935); (e) Wall and Glockler, *ibid.*, **5**, 314 (1937).

Since the top of the barrier is probably in the vicinity of 50 kcal. it is likely that there is a tunneling reaction for ethylene and that it has a rate in the tenth level

$$k'_{10} \sim 10^4\, e^{-23{,}000/kT} \tag{26}$$

We now consider the possibility for butene-2 tunneling. The moment of inertia I_r is larger and we expect a smaller rate. Using the same potential as for ethylene we calculate for the rate of tunneling in the 60th level.

$$k'_0 = 10^{-59.8}\, e^{-32{,}000/kT} \tag{27}$$

No reasonable change can be made in the potential to give an appreciable rate for a butene-2 tunneling reaction. The moments of inertia of the other compounds, maleic acid, stilbene, etc., are so much larger that it is quite safe to say that the influence of tunneling on these reactions is entirely negligible.

APPENDIX I

A. Interaction between the Singlet and Triplet States.—Spin-orbit interaction is the reason for the connection of singlet and triplet states. This force is rather weak for carbon atoms, and we shall estimate the magnitude from spectroscopic data. The term in the Hamiltonian is $e^2P/2m^2c^2 = e^2MS/2m^2c^2$ where M is the angular momentum operator and S is the spin operator. For two electrons $M = M_1 + M_2$ and $S = S_1 + S_2$. Neglecting the cross product terms (which are orders of magnitude smaller)

$$MS = M_1S_1 + M_2S_2 \tag{28}$$

Using the orbitals of Section II above it is found that $\int \psi_{\text{III}}^* P \psi_{\text{I}} d\tau = 0$. In order to have a non-vanishing interaction between these two states, certain higher orbitals must appear in either ψ_{I} or ψ_{III}. By an application of P on ψ_{I} we find that instead of ψ_{III} we must have

$$\psi'_{\text{III}} = \frac{1}{2\sqrt{2}} [(P_{\text{xa}}(1) + P_{\text{xb}}(1)) \{(P_{\text{xa}}(2) - P_{\text{xb}}(2)) + d(P_{\text{za}}(2) + P_{\text{zb}}(2))\} - (P_{\text{xa}}(2) + P_{\text{xb}}(2))\{(P_{\text{xa}}(1) - P_{\text{xb}}(1)) + d(P_{\text{za}}(1) + P_{\text{zb}}(1))\}]\, \alpha_1\alpha_2 \tag{29}$$

where d is different from zero. The integral $\int \psi'^*_{\text{III}} P \psi_{\text{I}}\, d\tau$ does not vanish. The interaction energy is

$$\frac{e^2}{2m^2c^2} \int \psi'^*_{\text{III}}\, P\psi_{\text{I}}\, d\tau = \frac{d}{4}\zeta \tag{30}$$

where

$$\zeta = \frac{h^2}{4\pi^2}\frac{e^2}{2m^2c^2} \int P^2_{\text{za}}(1)\, \frac{1}{r^3}\, d\tau$$

Now the constant d must be evaluated. From perturbation theory

$$d = \frac{\int \{P_{\text{xa}}(1) + P_{\text{xb}}(1)\} H' \{P_{\text{za}}(1) + P_{\text{zb}}(1)\}\, d\tau_1}{E_{\text{x}} - E_{\text{z}}} = 2\,\frac{H'_{\text{aa}} - H'_{\text{ab}}}{E_{\text{x}} - E_{\text{z}}} \tag{31}$$

where H' is the perturbation energy, E_{x} the energy of the orbital $P_{\text{xa}} + P_{\text{xb}}$, and similarly for E_{z}. H'_{aa} and H'_{ab} are the integrals defined by the equation.

If the substituents are neglected both of the integrals H'_{aa} and H'_{ab} vanish identically. The only perturbations which can give a non-vanishing d are interactions with the substituents. Further, for plane configurations of the molecule d vanishes because P_{x} is orthogonal to the plane. For the rotated configuration at which the crossing takes place, however, the groups on one carbon can perturb the other carbon sufficiently to cause a non-vanishing matrix element.

The integral H'_{ab} is zero to a good approximation since it involves an overlap between two carbon atoms. From Fig. 4 it is seen that the perturbations of the groups A and B are of opposite sign and thus tend to cancel each other. In ethylene itself, for example, H'_{aa} is identically zero. The part of H'_{aa} which depends upon A can be broken up into two parts one of which gives a fraction (depending upon the angle of rotation) of the interaction which a P function on a directed toward A would have; and the other gives a fraction of the interaction of a P function directed at right angles to the line joining a to A. These interactions have been estimated by means of Morse curves. It was assumed that the magnitude of the interaction when the P function is directed toward A is given by 0.4 of the Morse curve energy. The perpendicular interaction, in absence of better information, was taken as one-fifth this value.

$E_{\text{x}} - E_{\text{z}}$ was taken as 100 kilocalories/mole. The exact value of this difference is not known, but this estimate is most likely correct within a factor of two.

It was assumed that the triplet surface cut the singlet at 25 calories and the potential described in Section III was used to obtain the configuration of the molecules at the crossing point. The integral ζ was obtained from the singlet–triplet separation in the lowest state of carbon. As given by Bacher and Goudsmit this is 28 cm.$^{-1}$.

The values of d and the singlet–triplet interaction, ϵ, calculated in this manner are given in the table.

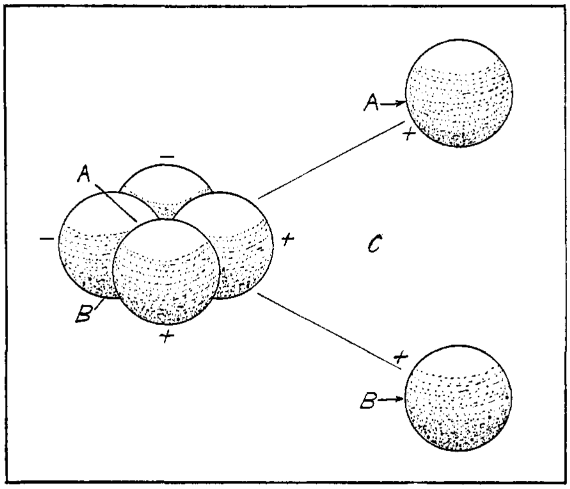

Fig. 4.—The charge distributions which give rise to the integral H_{aa}. Both carbon atoms and the A and B on the right are in the plane of the paper; A-B to the left is rotated by 30° to this plane,

	d	ϵ, cal.
Butene	0.0452	0.516
Maleic acid ester	.030	.342
Stilbene	.0584	.667

B. Calculations of ρ_1.—For small values of ϵ the formula for ρ_1 becomes

$$\rho_1 = \frac{4\pi^2\epsilon^2}{h\nu\,|S_i - S_f|} \qquad (32)$$

Taking $v = \dot{\theta} = 10^{13}$ radians per second and $|S_i - S_f|$ as 40 kilocalories we get

$$\rho_1 = 1.04 \times 10^{-6}\,\epsilon^2$$

where ϵ is given in calories. Using the ϵ values above we get the following values

Butene	2.76×10^{-7}
Maleic ester	1.22×10^{-7}
Stilbene	4.63×10^{-7}

APPENDIX II

The Matrix Element H'_{if}.—In Section IV we have used the quantity

$$(H'_{\mathrm{if}})_{\mathrm{n}} = \int \Phi^*_{\mathrm{in}}\, H'\, \Phi_{\mathrm{fm}}\, \mathrm{d}\tau = \int \psi^*_{\mathrm{I}}\, \theta^*_{\mathrm{in}}\, H'\, \psi_{\mathrm{III}}\, \theta_{\mathrm{fm}}\, \mathrm{d}\tau \qquad (33)$$

Except for the spin-orbit interaction ψ_{I} and ψ_{III} do not combine at all; so for H' we take the spin orbit operator of Appendix I.

$$\begin{aligned}(H'_{\mathrm{if}})_{\mathrm{n}} &= \int \psi^*_{\mathrm{I}}\, H'\, \psi_{\mathrm{III}}\, \mathrm{d}\tau_{\mathrm{el}} \int \theta^*_{\mathrm{in}}\, \theta_{\mathrm{fm}}\, \mathrm{d}\tau_{\mathrm{vib}} \\ &= \epsilon\, S_{\mathrm{nm}} \end{aligned} \qquad (34)$$

S_{nm} is the overlap of the wave functions for the torsional motion in the two different potentials. ϵ has been evaluated, so only S_{nm} must be calculated now.

We take the wave functions for the two potentials as

$$\left.\begin{aligned}\theta_{\mathrm{in}} &= N_{\mathrm{n}}\, e^{-\eta^2/2}\, H_{\mathrm{n}}(\mathrm{n}) \\ \theta_{\mathrm{fm}} &= \frac{1}{\sqrt{2\pi}}\, e^{im\theta}\end{aligned}\right\} \qquad (35)$$

The first of these is the wave function for a harmonic oscillator. $\mathrm{H_n}(\eta)$ is the n^{th} Hermitian polynomial and N_{n} is the normalization factor

$$N_{\mathrm{n}} = \left\{\left(\frac{\alpha}{\pi}\right)^{1/2} \frac{1}{2^n n!}\right\}^{1/2}$$

with $\alpha = 4\pi^2 I_r \nu_0/h$ and $\eta = \sqrt{\alpha}\theta$. I_r is the reduced moment of inertia for the torsional motion and θ is the angle of rotation.

The second function is just that for a rotator.

Using these functions it is quite simple to evaluate the overlap integral. The generating function for the Hermitian polynomial is now introduced

$$\sum \frac{1}{n!}\, H_{\mathrm{n}}\,(n)\, t^n = e^{n^2 - (t-n)^2} \qquad (36)$$

and to a high degree of approximation we obtain

$$S_{\mathrm{nm}} = \left\{\left(\frac{1}{\alpha\pi}\right)^{1/2} \frac{n!}{2^n}\right\}^{1/2} e^{-m^2/2\alpha} \sum_{j=0}^{\frac{n}{2} \text{ or } \frac{n-1}{2}} \frac{1}{j!}\, \frac{1}{(n-2j)!} \left(\frac{2i\,m}{\sqrt{\alpha}}\right)^{n-2j} \qquad (37)$$

The summation of j runs to the $n/2$ or $(n - 1)/2$ depending upon whether n is even or odd.

For butene-2 the reduced moment of inertia I_r is calculated as 1.08×10^{-39} sq. cm. Using the constants of the potential given earlier, α is found to be 60.345. The separation of levels in the singlet potential is 890 calories (as calculated); so the value of n is approximately 20. The values of S_{nm} oscillate from positive to negative as m increases, with an average value $\sim$0.05 as determined from the first ten values of m (see Table III).

TABLE III

m	$S_{20,\mathrm{m}}$
0	0.114
1	.0755
2	− .00862
3	− .0865
4	− .109
5	− .0627
6	.0245
8	.107
10	− .00369

For maleic ester the reduced moment of inertia is taken as 53×10^{-39} g. sq. cm. The separation of levels in the singlet potential is only 125 calories; so the appropriate value of n is $\sim$ 200. There are 100 terms in the series giving the values of $S_{200,\mathrm{m}}$ and so the actual calculation was not made, but apparently the values are approximately the same as those for butene.

If 0.05 is used as an average value for S_{nm}, the matrix elements, H_{if} are: maleic ester $0.3 \times 0.05 = 1.5 \times 10^{-2}$; butene $0.5 \times 0.05 = 2.5 \times 10^{-2}$.

It was pointed out previously that there cannot actually be free rotation in the triplet state in most cases. However, the magnitude of the overlap does not depend very critically on the particular wave function which was used for the triplet state. If this function is taken as a harmonic oscillator eigenfunction with a much smaller force constant than that for the singlet state essentially the same result is obtained. We shall make this calculation now. Taking for the triplet state

$$\theta_{\mathrm{fm}} = N_{\mathrm{m}} H_{\mathrm{m}}(\delta\eta)\, e^{-\delta^2\eta^2/2} \qquad (38)$$

Here $\delta = \sqrt{\alpha'}/\alpha$ and $\alpha' = 4\pi^2 I_r \gamma'_0/h$, the primes indicating the triplet state. The generating functions (equation 36) are introduced and the integration is carried out as before.

The values of S_{nm} are found as coefficients in a power series.

$$S_{\mathrm{nm}} = \sqrt{\frac{2\delta}{\delta_2 + 1}}\, \frac{\sqrt{n!m!}}{2^{\frac{n+m}{2}}} \sum_{l=1 \text{ or } 0}^{\mathrm{n \text{ or } m}} \frac{1}{e!}\left(\frac{4\delta}{1+\delta^2}\right)^l \frac{1}{i!}\left(\frac{1-\delta^2}{1+\delta^2}\right)^i \frac{1}{j!}\left(\frac{-(1-\delta^2)}{1+\delta^2}\right)^j \qquad (39)$$

The summation is to be made as follows. The largest value of l is the smaller of n or m, and l is summed over *alternate* integers to 1 or 0. For each value of l, i and j are determined

$$\begin{aligned} i &= (n - l)/2 \\ j &= (m - l)/2 \end{aligned} \qquad (40)$$

Taking $\delta = 100$, $n = 20$ values of S_{nm} are found to vary more regularly than for the rotator functions (Table IV). The origin for the triplet oscillator is at the same place as for the singlet, so odd and even states do not combine. The magnitude of these overlaps is just about the same as the ones reported above.

TABLE IV

m	$S_{20,m}$
0	0.0597
2	$-$ .0419
4	.0360
6	$-$ .0326
8	.0302
10	$-$ .0284

Summary

A model of the potential for rotation about the ethylenic double bond is presented and the possibilities for two types of isomerization reactions are discussed. One is an adiabatic reaction which has essentially the "normal" properties for first order reactions. The other is a non-adiabatic reaction which has a very small frequency factor. It is shown that this small factor arises from two causes: (1) the interaction between the two potential surfaces concerned is rather small; (2) only a few of the states in the final potential are available to the molecules in the initial potential. Absolute reaction rate expressions are given for the rates of these reactions and the calculated rate constants for the isomerization of maleic dimethyl ester and butene-2 (which react by the non-adiabatic mechanism) are in satisfactory agreement with experimental values.

The possibility for tunneling is considered and it is concluded that there is vanishingly small probability for this process.

PRINCETON, NEW JERSEY RECEIVED AUGUST 7, 1940

[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Thermal Data. XIV. The Heat Capacities and Entropies of Some Compounds Having the Peptide Bond

BY HUGH M. HUFFMAN

The peptide bond is of primary importance in the structure of proteins. As the initial step in an investigation of the energetics of this bond we have determined the heat capacities of glycylglycine, alanylglycine, leucylglycine, hippuric acid and hippurylglycine. These data have been utilized to calculate the entropies of these compounds.

Experimental

In principle the method of Nernst was employed with an aneroid calorimeter to determine the "true" specific heat. The details of the method have been described elsewhere[1] so that only a brief account need be given. In brief it consists of supplying, electrically, a measured amount of energy to the gold calorimeter containing the substance under investigation. To ensure rapid attainment of thermal equilibrium, the substance is pressed into dense pellets, about 2 mm. thick, and spaced along the centrally located thermocouple well by means of thin gold disks which are in good thermal contact with the walls of the calorimeter. The electrical measurements of current and voltage are made on a "White" double potentiometer by the proper use of accurately calibrated resistances. Time measurements are made by means of a calibrated stop watch. The temperature measurements are made by means of the White potentiometer in conjunction with a single junction copper–constantan thermocouple. This couple is periodically standardized against one of the couples calibrated in the investigation of Giauque, Johnston and Kelley.[2]

Materials.—The *dl*-alanylglycine was a commercial product obtained from Hoffmann–LaRoche. Nitrogen determinations by micro Kjeldahls gave 99.7% of theoretical. The ash content was less than 0.1%.

The *dl*-leucylglycine was given to us by K. Linderstrøm-Lang; according to his analytical data he found 100.1% of the theoretical carboxyl groups and 99.6% of the theoretical amino groups. Nitrogen analyses by micro Kjeldahls gave 99.8% of theoretical.

The hippuric acid, hippurylglycine and glycylglycine were "Analytically Pure" products obtained from the Amino Acid Manufacturers and were guaranteed to be not less than 99.5% pure.

The heat capacity data in terms of the defined conventional calorie (1 calorie = 4.1833 int. j.) are given in Table I. The entropies of these compounds have been calculated by a graphical integration of a plot of C_p against ln T over the experimental range and by the extrapolation method of Parks, Kelley and Huffman[3] from 0 to 90°K. The molal entropies of these compounds are given in Table II. We estimate that the accuracy of the experimentally determined quantities is 1% or better. It is not possible to make a reliable estimate of the uncertainty in the extra-

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(1) Parks, THIS JOURNAL, **47**, 338 (1925).

(2) Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

(3) Parks, Kelley and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).