EXPERIMENTAL DETERMINATION OF THE HEIGHT OF THE POTENTIAL BARRIER IN THE HYDROGEN BONDS OF BENZOQUINHYDRONE

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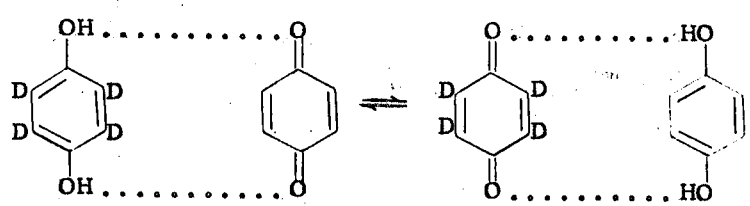
The problem of the position and mobility of the hydrogen atom in hydrogen bonds has not hitherto been closely studied. The potential curve of this atom may be represented as the sum of two intersecting curves forming two minima which are separated by a potential barrier. These minima correspond to two equilibrium positions, for example O—H . . . . . O and O . . . . . H—O and, especially at certain bond lengths, they can merge. The state of the hydrogen atom in hydrogen bonds is governed by the height of this potential barrier. If it is of a certain order of magnitude with zero vibration energy of the O—H (or alternatively of the X—H for the X—H . . . . . X bond), then the hydrogen atom very often moves from one position to another and hence is delocalized. At a high potential barrier the localization of this atom is maintained; such transitions as O—H . . . . . O⇌O . . . . . H—O are, however, possible (a type of tautomeric transformation), depending upon the height of the barrier which governs the energy of activation of this transformation. Finally, with a very high barrier the hydrogen atom is firmly fixed at one of the two atoms (or groups) linked by it.

The theoretical calculation of the height of the potential barrier in question for different hydrogen bonds has been carried out in a series of investigations with extremely conflicting results: from a few kcal/mole [1], for example 2, to 30 and more kcal/mole [2, 3, 4]. The majority of these calculations are based on questionable assumptions which deprive them of any quantitative reliability. This applies above all to the approximation of the potential curve of the X—H . . . . . X bond by the Morse function which is here invalid due to the great unharmonicity of the vibrations of the hydrogen bond itself [6]. For this reason the actual parameters selected for the calculation are very untrustworthy. This applies both to the identification of the frequencies, which has hitherto been a controversial point [7], and to the choice of bond lengths. Moreover, the calculated height of the barrier is greatly dependent on the given X—X distances, especially, on the equilibrium position of the hydrogen atom in the bond which, as we know, can still not be reliably measured. A change in the X—X distance by 0.2 A may change the calculated height of the barrier a hundredfold [2]. Furthermore, as was shown by M. L. Batuev [3], the height of the barrier is also highly dependent upon the nature of the end atoms or groups and differs completely from that of the isolated hydrogen bond to which, openly or indirectly, the majority of calculations relate. Finally, we have to remember that when the potential curve is asymmetric, the passage of hydrogen atoms through the barrier is accompanied by marked distortion of this curve due to rearrangement of the electron densities both inside the hydrogen bond and in other parts of the molecule.

We see from the foregoing data that the direct experimental determination of the height of the potential barrier in hydrogen bonds is a matter of considerable interest. Prior to the present investigation, it had never been undertaken. We made use of an isotopic method.

In previous researches one of us and G. P. Miklukhin [5] had shown that in benzoquinhydrone the hydrogen atoms of the hydrogen bonds remain near the hydroquinone nucleus so that the frequently propounded theory of oscillation of the hydrogen atom between two equilibrium positions or the theory of its delocalization is refuted by direct experiment in this case. Since up to now these researches were the sole direct experimental investigation of the problem under consideration, the question still remains open as to whether localization is a specific feature of the hydrogen bonds of benzoquinhydrone or whether it bears a general character. The observed localization of the hydrogen atom in hydrogen bonds points to a considerable height of the potential barrier between two minima corresponding to the two equilibrium positions of the hydrogen atom. This barrier (with accuracy down to zero energy) is equal to the energy of activation of the transformation:



(1)

which may be observed if one of the nuclei of the benzoquinhydrone molecule is labeled with deuterium, as was done in the cited investigations and as is indicated in the equation above.

In the previous investigations the possibility of slow transformation (equation 1) with a high activation energy was suggested. This is confirmed by the data below.

EXPERIMENTAL

The kinetics of reaction (1) may be studied with the help of deuterium because in the course of the reaction the nucleus of heavy hydroquinone is transformed into the nucleus of heavy quinone, while the nucleus of light quinone transformed into the nucleus of light hydroquinone. Consequently fractionation of the reaction product gives quinone containing heavy quinone in an amount which serves as a measure of the course of the reaction.

The benzoquinhydrone from heavy hydroquinone and ordinary quinone [5] were heated in quartz ampoules for a definite time at a given temperature and then separated into quinone and hydroquinone by fractional sublimation in high vacuum at 95°. Fractionation was complete after 45 minues, but after the first 15 minutes about 70% of the substance had been fractionated. The procedure differed from that previously described in that the operation was performed in a quartz vessel with small plugs of cotton wool. This change was dictated by the fact that glass catalyzes the reaction and was responsible for the poor reproducibility of our previous experiments.

In blank experiments with previously unheated quinhydrone, it was found that during the actual sublimation there is slow transfer of deuterium into the quinone, equal in our experimental conditions to 1.8%; the process shows good reproducibility when using identical amounts of material (0.3 g) and when the sublimation conditions are unchanged, as was the case in our investigation (see the first two experiments in Table 1). This correction is reduced in experiments with previously heated quinhydrone in accordance with transformation (1) which continued right up to the fractional sublimation. It is proportional to the degree of transformation before sublimation and it amounted in different experiments to 1.4 to 0.6% D.

Isotopic analysis was performed by the previously described procedure except that a microflotation method was applied which ensured an accuracy of 5% of the determined value and permitted the analysis of 0.04-0.05 g water. The initial content of deuterium in the hydroquinone nucleus was 25%.

In Table 1 are set forth the results of kinetic experiments. In addition to the observed percentage passage of deuterium into quinone x_1, the table gives the magnitude of x corrected for the transfer of deuterium during sublimation. The latter served as the basis of further kinetic calculations. As a check, the content of deuterium was determined also in the hydroquinone after fractionation. From the same table we see that both analyses in all cases are in sufficiently good agreement with each other.

TABLE 1

Duration of heating (min.)	Temp. (in °C)	Found % D			Corrected value of x	$-\ln(1-x/x_\infty)$
		in quinone (x_1)	in hydroquinone	sum		
0	—	1.8	103	104.8	—	—
0	—	1.8	104	105.8	—	—
109	107.6	6.7	91	97.7	5.3	0.1122
109*		5.6	94.8	100.4	4.1	0.0856
220		10.5	92	102.5	9.4	0.2080
248*		8.2	93.5	101.7	6.9	0.1486
38*	115.1	9.4	93.5	102.9	8.2	0.1792
38		7.3	—	—	6.0	0.1280
60		11.9	92	103.9	10.9	0.2458
82		11.6	—	—	10.6	0.2383
120		15.5	90	105.5	14.8	0.3510
164		15.1	85.4	100.5	14.4	0.3397
164*		17.3	85.8	103.1	16.6	0.4040
20*	119.8	8.5	92	100.5	7.2	0.1548
20		10.0	—	—	8.9	0.1960
58*		15.3	89.1	104.4	14.6	0.3455
58		15.5	89.3	104.8	14.8	0.3510
115		18.0	85.3	103.3	17.4	0.4278

TREATMENT OF RESULTS

Transformation (1) corresponds to a reversible monomolecular reaction obeying the equation:

$$-\ln(1-x/x_\infty) = Kt, \quad (2)$$

where $K = K_1 + K_2$ — the sum of the velocity constants of the forward and reverse reactions and x_∞ is the limiting equilibrium value of the magnitude x. Since the replacement of hydrogen by deuterium in the benzene ring cannot

* Heating was performed in nitrogen-filled ampoules.

Note. Duration of sublimation 45 minutes.

substantially influence the energetic and kinetic properties of the investigated system,* then $K_1 = K_2$ and $x_{\infty} = 0.5$.

The dependence of the magnitude of $-\ln(1 - x/x_{\infty})$ on the duration is represented by the experimental points in Fig. 1. We see from this that approximately up to $x = 0.1$, the kinetics of the process satisfactorily accord with equation (2). With more prolonged heating the transfer slows down and the deviation from the equation of the monomolecular action constantly increases. These deviations must be attributed to some secondary reaction whose nature we could not establish. Evidently, connected with this anomaly is another one which was observed in lengthier experiments whose results are set forth in Table 2. We see from this table that not once could values of x exceeding 0.3 be reached.

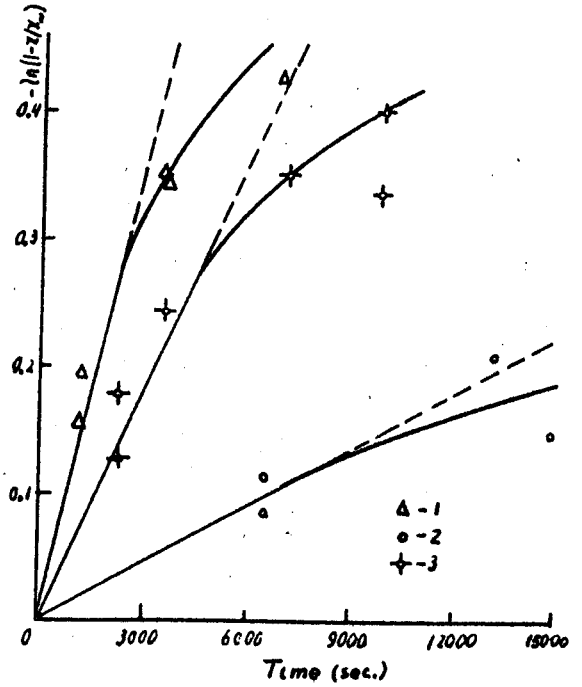


Fig. 1. Dependence of the velocity of transfer of deuterium from hydroquinone to quinone on the temperature. 1 - experiments at 119.8°; 2 - experiments at 107.6°; 3 - experiments at 115.1°

TABLE 2

Duration of heating (min.)	Temp. (in °C)	Found % D		
		in quinone	in hydroquinone	sum
60**	120°	27.4	74	101.4
1740**	120	26.5	73	99.5
180**	129-130	27.3	69	96.3
480**	129-130	26.8	71	97.8
2450***	120	26.0	75.8	101.8
1800***	115	20.6	77.2	97.8
2450****	120	—	29.8	—
1800****	115	85	17	102

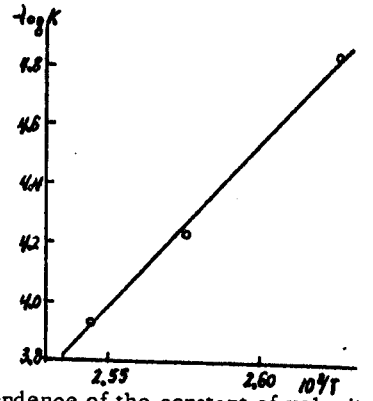


Fig. 2. Dependence of the constant of velocity of transfer of deuterium from hydroquinone to quinone on the temperature.

The further treatment of the experimental data was based on the fields in which these anomalies do not yet take effect, and in accordance with this we adopted for x_{∞} the value of 0.5***** indicated above. The analytically interpolated straight lines of Fig. 1, give the following velocity constants K in sec.$^{-1}$:

Temperature	107.6	115.1	119.8°
K	$0.89 \cdot 10^{-3}$	$3.60 \cdot 10^{-3}$	$7.08 \cdot 10^{-3}$.

The scatter of the experimental points introduces a certain arbitrariness into the choice of slope of the straight lines, but we can readily convince ourselves that the different methods of interpolation, compatible with the experimental data, do not change the value of the activation energy by more than a few percent. We see from Fig. 2 that the values of $\log K = f(1/T)$ fall fairly consistently on a straight line for which we obtained (by the method of least squares):

$$\log K = 24.070 - 11.00 \cdot 10^3 \, 1/T. \qquad (3)$$

Application of the usual equation with a Boltzmann distribution of energy from two quadratic terms would give, according to (3)

$$K = 1.18 \cdot 10^{24} \, e^{-50314/RT}$$

* This is confirmed by the data of the preceding research [5] and by the data in Table 2.

** Heating in glass. *** Heating in quartz. **** Quinhydrone from ordinary hydroquinone in heavy quinone.

***** Repetition of the calculation with $x_{\infty} = 0.25$ does not seriously influence the result: the velocity constants are reduced by a factor of 2, while the activation energy increases by less than 2 kcal/mole.

However, the value of 50.3 kcal/mole calculated by this method for the activation energy does not correspond to the actual value due to the application of the simplified energy distribution formula with two quadratic terms for the monomolecular decomposition reaction of such a complex molecule as quinhydrone in which the energy is distributed along many vibrating degrees of freedom. A sufficiently close approximation in such cases is obtained with the equation:

$$K = A\frac{(E/RT)^{m-1}}{(m-1)!}e^{-E/RT} = P \cdot e^{-E/RT} \qquad (4)$$

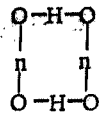
where P is a fore-exponential factor, E is the activation energy and m is the number of vibrating degrees of freedom of the activation energy. It has already been successfully used for the kinetics of a series of monomolecular reactions [8]. For its three parameters we have only two variables: the velocity constant and its temperature coefficient. The relation between the activation energy and the number of degrees of freedom may be directly obtained by comparison of the derivatives for 1/T from (3) and (4).

$$E/RT^2 - \frac{m-1}{T} = 11.00 \cdot 10^3 \cdot 2.3026,$$

from which, for a mean value of T = 387°, we find*

$$E = 50314 + 768.6\,(m-1). \qquad (5)$$

For unequivocal determination of the value of the activation energy, the number of degrees of freedom m must be given in addition.** It is plausible to assume that in the benzoquinhydrone molecule the internal vibrations of the nuclei (n) interact weakly with the vibrations of the atoms participiating in the formation of hydrogen bonds. This molecule must then be regarded as a system of 8 vibrating centers:



having m = 8 · 3 − 6 = 18* of freedom. According to (5) we get E = 63380.

The value found for the activation energy, corresponding to the choice of the number of m, can be regarded as close to the upper limit of the actual value. With a smaller number of degrees of freedom, the latter may be lower by several kcal/mole. The scatter of the experimental points and other sources of error do not introduce an inaccuracy which should exceed the indicated magnitude.

Having substituted in (4) the magnitude log K = −4.354, calculated from (3) for the indicated mean temperature, we find log P = 24.11 + 0.434 (m − 1) or 31.49 for m = 18; hence:

$$K = 3.17 \cdot 10^{13}\frac{(63380/RT)^{17}}{17!}e^{-63380/RT}$$

This equation gives values for K which differ from the experimental ones by not more than 15%.

The high value of the fore-exponential factor, equal to $3 \cdot 10^{31}$ sec^{-1} may depend both on the fact that — in contrast to gaseous reactions — in the crystalline lattice the activation is effected by a transfer of vibratory energy, and on a possible chain mechanism of the propagation of process (1) in this lattice.

The comparatively high value of the activation energy (in round figures 63 kcal/mole) is easily accounted for by the reaction requiring the transfer of an atom of hydrogen in two hydrogen bonds with simultaneous far-reaching rearrangement of the remaining bonds. There is every reason to believe that both transitions take place in a single elementary act (in the kinetic sense). This is in accord with the inability (up to now) to detect the decomposition of benzoquinhydrone to the correspondence semiquinones [9]***

* The dependence of log K on 1/T, according to (4), does not appreciably depart from linearity in the considered temperature range.

** For gaseous reactions it is usual to put the magnitude of A as that pressure below which a monomolecular reaction degenerates into a second order reaction [8]. This gives, in principle, the supplementary condition determining the value of m. Such a procedure is evidently here not applicable and its reliability is generally doubtful.

*** Decomposition to semiquinones should also have been manifested in the cited previous investigations and should have caused a more or less far-reaching delocalization of the hydrogen atoms.

Consequently, the height of the potential barrier of the hydrogen bond in benzoquinhydrone is equal to half of the activation energy, i.e. about 32 kcal/mole from the zero level of the valence vibration of OH or about 37 kcal/mole from the bottom of the potential trough of this bond.

For the reasons indicated above, a comparison of the values that we found with the theoretically calculated values do not present great interest, especially since the latter relate to other hydrogen atoms. Attention may be drawn, however, to two recent researchers, M.I. Batuev [3] calculated that the potential barrier of the OHO bond changes from 33.4 kcal/mole for water and 24 kcal/mole for propionic and higher saturated acids to 4.8 kcal/mole for crystalline β-oxalic acid. This author notes that his results agree with the localization of hydrogen bonds in benzoquinhydrone found in a previous investigation [5]. M. A. Kovner and V. A. Chuenkov [4] replaced for Morse function by another one which gave a rounded peak of the potential barrier, lowering its value by 8 kcal/mole. For formic, acetic and isovaleric acids they obtained 22-26 kcal/mole for one interpretation of the spectral frequencies and considerably lower values of 14-16 kcal/mole for other interpretations. They regard the last values as the more probable. We see from these data how strongly the calculated results are influenced by the identification of the spectral frequencies of the hydrogen bonds; this identification still remains uncertain. For the case considered in this study, the uncertainty is aggravated by the lack of X-ray and spectrographic data for benzoquinhydrone and its components. Consequently, we refrain from theoretical calculations aiming at a comparison with the experimental value found in this investigation.

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SUMMARY

1. With the help of deuterium a study was made of the passage of hydrogen atoms from hydroquinone nucleus into the quinone nucleus in the hydrogen bonds of benzoquinhydrone.

2. The energy of activation found for this process was about 63 kcal/mole, which corresponds to a height of the potential barrier of 32 kcal/mole in these bonds, reckoned from the level of zero energy of the valence vibrations of OH.

3. This first experimentally determined value of the potential barrier of the hydrogen bond was compared with the theoretically calculated values which only give a qualitative result due to the uncertainty of the parameters on which they are based.

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