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APPLICATION OF THE KINETIC ISOTOPE EFFECT OF TRITIUM TO THE INVESTIGATION OF THE MECHANISM OF HYDROGEN SUBSTITUTION AND TRANSFER REACTIONS

F.S. Yakushin

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I. INTRODUCTION

The velocity of a reaction is affected when the atom involved is replaced by its isotope in the molecule if the bond between this atom and another element is ruptured during the rate-determining stage of the reaction. The effect is expressed as the ratio of the rate constants for

the molecules containing the different isotopes, and is called the kinetic isotope effect. Theoretical calculations of kinetic isotope effects and their experimental determination have been widely studied. The latter is of special importance, because sufficiently accurate theoretical calculations are possible only for comparatively few reactions. Study of kinetic isotope effects provides information on reaction mechanisms, the nature of the transition state, etc. Such investigations have been carried out mainly with isotopes of hydrogen, nitrogen, and carbon, and to a lesser extent with those of oxygen, chlorine, etc. Several reviews[1-10] have been published on kinetic isotope effects.

The present review is concerned with recent work in which tritium has been used to study the mechanism of heterolytic reactions involving the substitution, exchange, and transfer of hydrogen. This radioactive hydrogen isotope has the advantage over deuterium that its greater mass results in a larger kinetic isotope effect (where it is observed). Use of tritium and deuterium together enables the kinetic isotope effect in hydrogen exchange to be investigated.

The concentrations of tritium used to investigate reaction mechanisms should be small, since otherwise its natural β-radiation may affect the course of the reaction[11].

II. THEORY OF THE KINETIC ISOTOPE EFFECT

Theoretical analysis of the kinetic isotope effect is often confined to a consideration of the most important factor responsible for its appearance, which is the difference in the zero-point energies of the bonds formed by the isotopes of a given element with some other atom. The potential-energy curves for the bond with protium will then generally be identical with the curves for the bond formed by the same atom with deuterium or with tritium: *i.e.* the classical activation energies for the reactions of such molecules can be regarded as identical. The difference in reaction rates is due to the difference in vibrational energy of the lowest levels in the initial and the transition states.

At or near room temperature almost all bonds are in the lowest energy state, and the vibrational energy is approximately the same as at the absolute zero, *i.e.* E^0. The zero-point energy is related to the vibration frequency ν_i of a bond as follows.

$$E^0 = \frac{1}{2} \Sigma h\nu_i . \qquad (1)$$

For a harmonic oscillator, the vibration frequency of the bond is

$$\nu_i = \frac{1}{2\pi} \sqrt{\frac{f}{m^*}} , \qquad (2)$$

where f is the force constant and m^* the reduced mass.

For comparatively heavy molecules containing protium, deuterium, and tritium, the reduced masses may be regarded as in the proportions

$$m_H^* : m_D^* : m_T^* = 1 : 2 : 3, \qquad (3)$$

if it is assumed that the force constants of bonds formed by different isotopes are identical.

Thus the zero-point energy for a bond with deuterium will be less by a factor of about $\sqrt{2}$, and that for a bond with tritium by a factor of about $\sqrt{3}$, than the value for a bond with protium.

The true activation energy is defined by the relation

$$E^a = E_{cl} + E_{\neq}^0 - E^0, \qquad (4)$$

where E_{cl} is the classical activation energy, E^0 the zero-point energy of the bond in the initial state, and $E_{\neq}^0$ the zero-point energy in the transition state.

The difference in activation energy for the rupture of X–H and X–T bonds will be

$$E_{X-H}^a - E_{X-T}^a = [(E_{\neq}^0)_{X-H} - (E^0)_{X-H}] - [(E_{\neq}^0)_{X-T} - (E^0)_{X-T}]. \qquad (5)$$

The first difference on the right-hand side of this equation is smaller than the second difference, and therefore $E_{X-H}^a < E_{X-T}^a$: *i.e.* the activation energy for rupture of a bond with protium will be less than that for the bond with tritium.

Fig. 1 shows the maximum difference in activation energy, and hence the maximum isotope effect, assuming that the bond in question is completely ruptured in the transition state.

An example of the way in which the effect of the difference in the zero-point energies of bonds on reaction velocities is estimated is provided by Melander's approximate calculation[12] for ordinary benzene and benzene in which a hydrogen atom has been replaced by an atom of deuterium or of tritium. The basic assumption is that all bonds other than that directly involved in the reaction, which is assumed to be ruptured, are unchanged in the transition state. The difference in activation energy, and hence in reaction velocity, will then be determined only by the difference in the zero-point energies of the C–H, C–D, and C–T bonds in the initial state. For the case of protium and tritium in benzene molecules, this difference can be written as follows:

$$E_{C-T}^0 - E_{C-H}^0 = \frac{1}{2} Nh(\Sigma\nu_{C_6H_6} - \Sigma\nu_{C_6H_5T}) = \frac{1}{2} Nhc(\Sigma\omega_{C_6H_6} - \Sigma\omega_{C_6H_5T}), \qquad (6)$$

where $\omega_{C_6H_6}$ and $\omega_{C_6H_5T}$ are the wave numbers of the initial states of the C–H and C–T bonds respectively. The wave numbers corresponding to an aromatic C–H bond are 3000, 1100, and 700 cm^{-1}. Since it follows from Eqn. (2) that, with appropriate assumptions,

$$\omega_{C-T} : \omega_{C-H} \simeq 1/\sqrt{3} , \qquad (7)$$

then

$$E_{C-T}^0 - E_{C-H}^0 = \frac{1}{2} (1-1/\sqrt{3}) \Sigma'\omega_{C_6H_6}, \qquad (8)$$

where Σ' relates only to the single C–H bond. Hence

$$E_{C-T}^0 - E_{C-H}^0 = \frac{1}{2} (1-1/\sqrt{3})(3000+1100+700) = 1020\ cm^{-1}. \qquad (9)$$

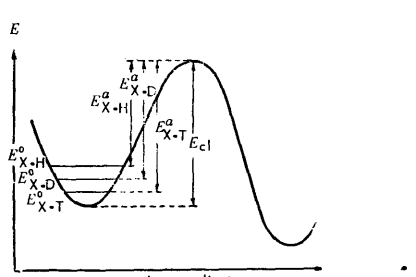


Fig. 1. Relation between the classical activation energy and zero-point bond energies of isotopic molecules.

A similar calculation for deuterium gives

$$E^0_{C-D} - E^0_{C-H} = \frac{1}{2}(1-1/\sqrt{2})\,\Sigma'\omega_{C_6H_6} = 703 \text{ cm}^{-1}, \quad (10)$$

which agrees well with experimental results obtained for deuterated benzenes (Table 1)

In energy units

$$E^0_{C-T} - E^0_{C-H} = \frac{1}{2} NhC \cdot \Sigma'\omega_{C_6H_6} = 2900 \text{ cal mole}^{-1}. \quad (11)$$

The ratio of the Arrhenius exponential functions of the rate constants for the tritium–protium pair at room temperature is as follows:

$$\frac{e^{-E^0_{C-T}/RT}}{e^{-E^0_{C-H}/RT}} = e^{-\frac{2900}{1300}} = 1/125. \quad (12)$$

The corresponding ratio for the deuterium–protium pair under the same conditions and with the same assumptions is approximately 1/29.

The main assumptions in calculations of the kinetic isotope effect relate to the nature of the reactive bond in the transition state. It is supposed in one of the limiting cases that this bond is completely ruptured, *i.e.* in the transition state the isotopic atom is at an infinite distance from the rest of the molecule. Calculations by Bigeleisen[13] for such a case give values for the maximum isotope effect at room temperature of 60 for the proton–tritium pair and 18 for the protium–deuterium pair.

In the other limiting case, in which the state of the reactive bond remains about the same in the transition state as in the initial state, calculations give the following ratios of the rate constants for "light" and "heavy" molecules, depending on their mass:

$$k_H/k_D \simeq \sqrt{\frac{\dot{m}_D}{\dot{m}_H}} \simeq \sqrt{2} \quad (13)$$

and

$$k_H/k_T \simeq \sqrt{3}. \quad (14)$$

Real conditions represent an intermediate case in which the reactive bond is not completely ruptured in the transition state, but is only more or less deformed.

The difference in the zero-point energies of the bonds in the transition state cannot in general be neglected. Its effect is to diminish the maximum isotope effect. The ratio of the rate constants is affected also by interaction with the solvent, which is different for isotopic substrate molecules. This interaction results in different degrees of polarisation of the reactive bonds, which affect the magnitude of the kinetic isotope effect[4,12,14]. Furthermore, with hydrogen atoms a non-classical penetration of the energy barrier (the tunnel effect) is possible. Bell[15] showed its effect on the velocity-constant ratio for several reactions involving hydrogen transfer. In some cases this effect can be allowed for in the theoretical calculation. In general it is small and decreases on passing from hydrogen to deuterium and tritium.

TABLE 1.

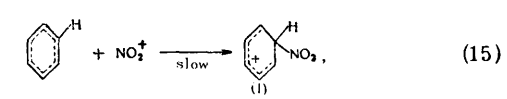
Compound	$\frac{1}{2}\Sigma\omega$, cm^{-1}	ΔE^0, cm^{-1}
Benzene	21536	
Monodeuterobenzene	20838	698
1,4-Dideuterobenzene	20172	666
1,3,5-Trideuterobenzene	19506	666
1,2,4,5-Tetradeuterobenzene	18801	705
Hexadeuterobenzene	17431	2×685

Depending on these circumstances, the magnitude of the kinetic isotope effect can vary between quite wide limits. Replacement of protium by deuterium in a reactive bond X–H usually results in a decrease in reaction velocity by a factor of 3–8, and with replacement of protium by tritium the corresponding factor is 6–20 at the rate-determining stage. Thus an estimate of the magnitude of the kinetic isotope effect must as far as possible take into account all the following factors: isotopic mass, temperature, character of bonds in the transition state, *i.e.* in effect the structure of the latter, etc. Otherwise, such an estimate is difficult, and can be carried out only by analogy with similar systems which have already been investigated, or by using hypothetical models of the transition state, which frequently yields the correct order of magnitude for the kinetic isotope effect.

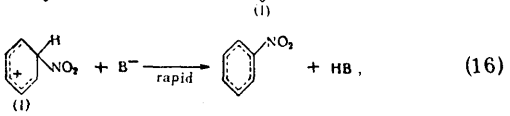
III. KINETIC ISOTOPE EFFECT OF TRITIUM IN ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS AND IN THE ACID EXCHANGE OF HYDROGEN

Two methods have been used for the experimental determination of the kinetic isotope effect, the first, a comparison of the experimental rate constants for the same reaction carried out with the usual and the isotopic compounds, and the second, undoubtedly the more accurate, a determination of the change in the isotopic composition of substrate molecules or reaction products corresponding to a definite fractional change during the reaction. Appropriate relations between these quantities have been obtained for various cases[16–18] and refs.5 and 12 contain an analysis of the range of application of such relations depending on the conditions of measurement.

1. Nitration. Melander[19,20] used data on the kinetic isotope effect to determine the mechanism of several reactions involving the electrophilic substitution of hydrogen in aromatic compounds. The reaction which was investigated most thoroughly was the liquid-phase nitration of aromatic compounds. The nitrating agent is the nitronium ion NO_2^+, whose existence has been demonstrated by many investigators[21,22]. A detailed study of this reaction led to the conclusion that it occurs in two stages:



(15)



(16)

where B^- represents a base which combines with the proton. Melander[20] tested this scheme experimentally by measuring the kinetic isotope effect in the nitration of a series of aromatic compounds labelled with tritium. The presence of tritium in the aromatic molecule was found to have no appreciable effect on the reaction velocity with any of the compounds investigated (benzene, bromobenzene, *o*-, *m*-, and *p*-toluene, napthhalene, etc.). It can be seen from Table 2 that the velocity-constant ratio k_T/k_H is close to unity at 350°K.

TABLE 2.

Compound	Position	Lower limit of k_T/k_H
Benzene	—	0.84
Nitrobenzene	3	0.74
Toluene	2	0.85
Bromobenzene	2	0.78
p-Bromonitrobenzene	2	0.81
Naphthalene	α	0.77

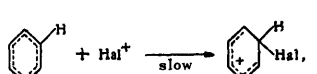
No isotope effect has been detected by other investigators[23] in the nitration of benzene containing ~91% of monodeuterobenzene.

To explain the absence of an appreciable kinetic isotope effect, the investigators assume that the rate of nitration is apparently determined, not by the rupture of a C–H bond attached to the aromatic ring, but by the addition of a nitronium ion with formation of the intermediate complex (I), the structure of which is similar to that postulated by Wheland[24]. Decomposition of this complex with the splitting off of a proton takes place rapidly†.

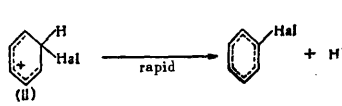
The influence of the polarity of the solvent on the rates of formation and disappearance of the nitronium ion also agrees with a two-stage mechanism for nitration. The solvent effect on the kinetics of the process casts doubt on the possibility of nitration by a termolecular mechanism:

$$NO_2^+ + Ar{-}H + B^- \rightarrow [NO_2^+ \ldots Ar \ldots H \ldots B^-] \rightarrow ArNO_2 + HB. \quad (17)$$

2. Bromination. Study of the kinetic isotope effect in the bromination of aromatic compounds is complicated by simultaneous hydrogen exchange between the aromatic compound and the hydrogen bromide formed when metal bromides are used as catalysts[12]. If, however, iodine is used as catalyst, the exchange takes place slowly, and the velocity-constant ratio for the dibromination of tritiated benzene and isomeric bromobenzenes at 85° ± 2° has been found to differ only slightly from unity. This indicates that, as in the case of nitration, the rate of bromination is probably not controlled by the proton removal from a carbon atom of the aromatic ring. This conclusion is consistent with the scheme of aromatic halogenation suggested by Robertson *et al.*[26]:



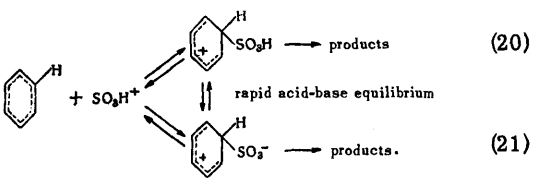
(18)



(19)

The intermediate complex (II) is assigned by Melander a structure similar to that of the complex (I).

3. Sulphonation. In contrast to the above reactions, the sulphonation of bromobenzene and *p*-bromotritiobenzene with oleum (some of the experiments were carried out in the presence of nitrobenzene as solvent) showed a slight isotope effect ($k_T/k_H = 0.55 \pm 0.09$ at 0°)[27]. This effect was later shown[28] to change very little when the temperature was raised from 0° to 50°. The reaction is assumed to have a two-stage aromatic electrophilic substitution mechanism, like those of nitration and halogenation, the difference in the rates of sulphonation of ordinary and tritiated molecules arising in the second stage, elimination of a proton in the transition state, which is partly rate-determining. The overall reaction scheme is as follows:



(20)

(21)

In contrast to nitration and bromination in the presence of iodine, the first stage in sulphonation, consisting in the attack of the sulphonating agent on the aromatic molecule, is reversible, and a quasi-stationary state can be assumed between the intermediate complex and the starting materials[7]. The velocity of the reaction

$$Ar{-}H + X^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar^+\!\!\begin{array}{l}\diagup X\\ \diagdown H\end{array}, \quad (22)$$

$$Ar^+\!\!\begin{array}{l}\diagup X\\ \diagdown H\end{array} + B \xrightarrow{k_2} Ar{-}X + HB^+, \quad (23)$$

can then be written, according to Bodenstein,

$$v_1 = k_1[ArH][X^+] = v_{-1} = k_{-1}\left[Ar^+\!\!\begin{array}{l}\diagup X\\ \diagdown H\end{array}\right] + k_2\left[Ar^+\!\!\begin{array}{l}\diagup X\\ \diagdown H\end{array}\right][B], \quad (24)$$

where v_1 and v_{-1} are the rates of formation and consumption of the intermediate complex.

Hence we find that

$$\left[Ar^+\!\!\begin{array}{l}\diagup X\\ \diagdown H\end{array}\right] = \frac{k_1[ArH][X^+]}{k_{-1} + k_2[B]}. \quad (25)$$

Representing the rate of formation of the final product by the equation

$$\frac{d[ArX]}{dt} = k_2\left[Ar^+\!\!\begin{array}{l}\diagup X\\ \diagdown H\end{array}\right][B], \quad (26)$$

and substituting for $[Ar^+HX]$ in Eqn. (26) from (25), we obtain

$$\frac{d[ArX]}{dt} = \frac{k_2k_1[B]/k_{-1}}{1 + k_2[B]/k_{-1}}[ArH][X^+]. \quad (27)$$

Inspection of this equation shows that, when k_{-1} is small, the denominator becomes $k_2[B]/k_{-1}$, and Eqn. (27) then takes the form

$$\frac{d[ArX]}{dt} \simeq k_1[ArH][X^+], \quad (28)$$

whence it follows that no isotope effect will occur on replacement of protium by deuterium or tritium in the Ar–H molecule, since only the rate constant k_2 is affected by such substitution. In the other extreme, when k_{-1} is large, the rate of the process will be roughly proportional

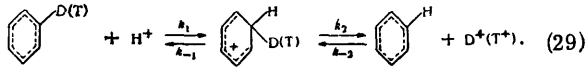
† Hammond[25] remarks that such a conclusion is not always necessary (see later, p.128).

to the rate constant k_2, and a kinetic isotope effect should then appear. This is evidently the case when an isotope effect was observed in sulphonation, *i.e.* the second stage is not too rapid compared with the reverse reaction of the first stage. A similar phenomenon has been noted by Zollinger[7] with azo-coupling, where a still greater isotope effect was observed when protium was replaced by deuterium in an aromatic molecule. In his view this effect, and other observations, is consistent with a two-stage mechanism of electrophilic hydrogen substitution [see scheme (22)–(23)], provided that a quasi-stationary stage is present.

Notable difficulties arise in the investigation of the isotope effect in sulphonation — absence of a homogeneous reaction system, formation of side-products if the solvent is nitrobenzene, and finally the possibility of hydrogen exchange.

4. Acid hydrogen exchange. The combined use of tritium and deuterium enables us to study the kinetic isotope effect in hydrogen exchange. Several examples showing the close connection between acid hydrogen exchange and electrophilic hydrogen substitution in aromatic compounds have been examined in detail in Shatenshtein's book[29].

The treatment of the kinetic isotope effect observed in reactions involving acid hydrogen exchange in aromatic compounds takes account of the similarity of their mechanism to that of chemical reactions involving electrophilic hydrogen substitution. Melander and Olsson[30,31] measured the effect of the difference in the rates of hydrogen exchange in deuterated and tritium-labelled benzene and isomeric toluenes in 80% sulphuric acid at 25°. They describe the process of hydrogen exchange using a two-stage mechanism similar to that adopted for the electrophilic substitution of hydrogen



(29)

According to such a scheme, the magnitude of the kinetic isotope effect in an exchange reaction involving deuterium or tritium will depend on the ratio of the velocity constants:

$$k = \frac{k_1 k_2}{k_{-1}+k_2} = \frac{k_1}{k_{-1}/k_2 + 1} . \qquad (30)$$

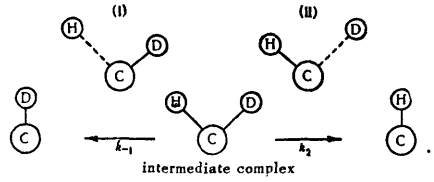
Comparison of the rate constants for the exchange of tritium and deuterium yields the ratio

$$k_T/k_D = \frac{(k_{-1}/k_2)_D + 1}{(k_{-1}/k_2)_T + 1} , \qquad (31)$$

it being assumed that replacement of deuterium by tritium does not appreciably affect the rate of the first stage, defined by the constant k_1 [*i.e.* that $(k_1)_T/(k_1)_D = 1$]. Thus the observed isotope effect will be determined by k_{-1}/k_2, the ratio of the velocity constant for the splitting off of protium to that for the splitting off of deuterium or tritium. The value of k_T/k_D can be roughly estimated if the intermediate complex is assumed to behave as a normal molecule. Actually, the usual value of k_D/k_H at room temperature is $\frac{1}{4}$, *i.e.* in this case $(k_{-1}/k_2)_D = 4$. The corresponding value for $(k_{-1}/k_2)_T$ can be obtained from the relation

$$k_H/k_T = (k_H/k_D)^{1.44}, \qquad (32)$$

deduced by Swain *et al.*[32] and extended by Melander[33] and Olsson[34] to isotopic hydrogen exchange in an acid medium, where the intermediate complex is supposed to contain both hydrogen isotopes. The isotope effect will be determined mainly by the vibrations of the carbon–hydrogen bonds in the transition states (I) and (II), and will not depend on the vibrations of bonds in the intermediate complex[35], which is common to both reactions:



In this model of acid hydrogen exchange C represents the active centre and a carbon atom in the aromatic ring; the broken line represents the bond which is ruptured in the transition state. The relation obtained between the protium–tritium and protium–deuterium isotope effects,

$$(k_{-1}/k_2)_T = (k_{-1}/k_2)_D^{1.44}, \qquad (33)$$

gives $(k_{-1}/k_2)_T = 4^{1.44} = 7.4$. A value of 0.60 is then obtained for the ratio k_T/k_D [from Eqn. (31)]. The value obtained experimentally agrees with this estimate (Table 3)‡.

The relative rates of exchange for tritium and deuterium in the *ortho*-, *meta*-, and *para*-positions in toluene are then

47 : 1 : 41 and 51 : 1 : 46.

No generally accepted view yet exists as to the detailed mechanism of the acid exchange of hydrogen in aromatic compounds. In Melander's opinion the intermediate product which is formed has the structure of a σ complex (see above scheme). The carbon atom at which substitution takes place is linked with other atoms by four sp^3 bonds. Two π electrons are involved in the formation of one of them, and the remaining π electrons form a pentadiene system. Satchell[36] postulates the presence, in the exchange with sulphuric acid, of at least three stages with two types of intermediate complexes: the proton first interacts with all the ring π electrons to form an intermediate π complex:

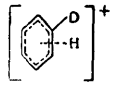


TABLE 3.

Isotopically substituted compound	k_T/k_D
Toluene, *ortho*-position	0.53
Toluene, *meta*-position	0.59
Toluene, *para*-position	0.52
Benzene	0.65

‡ Olsson[34] gives more accurate values for the ratio k_T/k_D under the same conditions, but the general character of the dependence of k_T/k_D on the position of the hydrogen in the ring remains the same.

This then rearranges to a σ complex, the decomposition of which results in formation of the products of the exchange.

According to Gold *et al.*[37], the experimental values of the kinetic isotope effects can be explained both by Melander and Olsson's scheme and by that given by Gold and Satchell. The rate of exchange of tritium in the *o*-tritio-*p*-cresol molecule with aqueous sulphuric acid is less by a factor of 2–3 than the rate of exchange of deuterium in the corresponding deutero-compound. On the basis of the reaction mechanism

$$H_3O^+ + Ar{-}H^* \underset{-1}{\overset{1}{\rightleftarrows}} (H\ldots Ar - H^*)^+ \underset{+H_2O}{} \overset{2}{\rightleftarrows} (H - Ar\ldots H^*)^+ \underset{+H_2O}{} \rightarrow H{-}Ar + H^*H_3O^+, \quad (34)$$

these investigators explain the difference in the rates of exchange of deuterium and tritium by different degrees of weakening of the bond with the hydrogen isotope which is split off at the slow stage.

The great influence exerted by the nature of the substrate and by the reaction medium on the character of the bonds in the transition state has been noted above, and these can also affect the magnitude of the kinetic isotope effect. Melander and Olsson[30] pointed out that the decrease in reactivity is accompanied by some decrease in the kinetic isotope effect (see Table 3). Thus the value of k_T/k_D for the *ortho*-position in toluene is 0.53, while for the less reactive *meta*-position this ratio is 0.59. The velocity-constant ratios for the exchange of tritium and deuterium in the *para*-position of toluene compared with benzene differ still more (0.52 and 0.65 respectively). The ratio of the velocity constants for the exchange of the *para*-hydrogen in toluene and of a hydrogen atom in benzene with sulphuric acid is 200-300. In order to obtain a more reliable test of the dependence of the isotope effect on the reactivity of a fixed position in the molecule, Östman and Olsson[38] used thiophen, since the rates of exchange of hydrogen atoms in positions 2 and 3 in its molecule differ by a factor exceeding 900[39]. With 57% sulphuric acid at 24.6° the values obtained for k_T/k_D were 0.51 in position 2 and 0.59 in position 3. Thus the same kind of variation of the kinetic isotope effect with reactivity is observed as in the above work[30]. For hydrogen exchange with sulphuric acid, differences in reactivity among non-equivalent positions are to a considerable extent levelled out. To study this effect, it would probably be more suitable to use liquid hydrogen bromide, which Shatenshtein *et al.*[29,40] have shown to be a differentiating solvent in the acid exchange of hydrogen.

5. Some difficulties in the interpretation of reaction mechanisms on the basis of the kinetic isotope effect. Hammond[25] remarks that a very small isotope effect in the electrophilic substitution of hydrogen with the intermediate formation of a σ complex is still not a definite proof that the reactive C–H bond is not ruptured in the rate-determining stage. In his opinion a small effect can also be observed when the proton loss is preceded by a very slight weakening of the C–H bond in the intermediate complex. Such a conclusion differs from those of Melander[3] with regard to the isotope effect in the nitration of aromatic compounds.

Other investigators have observed that substitution of a heavy isotope for hydrogen in an aromatic compound has different effects on the rate of halogenation depending on the nature of the compound, the halogenating agent, and the medium.

Thus Vainshtein and Shilov[41] found that, whereas the iodination of some aromatic amines shows no isotope effect, with others it is small (k_H/k_D = 1.4) or considerable (k_H/k_D = = 4), the latter value being obtained also in the iodination of phenol[42]. Farrell and Mason[43] found a value of 1.8 for this ratio in the bromination of dimethylaniline with bromine in sulphuric acid at 25°. They point out that the character of the bond in the transition state depends on the nature of the aromatic molecule which is attacked and on the substituting reagent employed. Myhre[44] found that replacement of hydrogen by tritium in the bromination of 1,3,5-tri-t-butylbenzene in the presence of silver perchlorate and perchloric acid in the acetic acid–dioxane–bromine system lowers the reaction velocity by a factor of approximately 10. Because of this and the absence of an isotope effect in the bromination of benzene in the presence of iodine as catalyst[12] or with hypobromous acid[45], he suggests that the velocity-constant ratio is affected by a steric factor. The great bulk of the substituent *ortho* to the site at which hydrogen is substituted tends to make the second stage in the general scheme of electrophilic substitution [Eqns. (22) and (23)] become rate-determining.

Existing measurements of the kinetic isotope effect in aromatic halogenation do not yet permit a definite relation between the magnitude of the effect and the factors which affect this reaction to be formulated. As Vainshtein and Shilov[46] have shown, such a relation is difficult to discover even in a study of a single reaction, such as the bromination of aromatic amines.

IV. KINETIC ISOTOPE EFFECT OF TRITIUM IN METALLATION AND HYDROGEN EXCHANGE WITH A BASE

Shatenshtein and his collaborators[29] have repeatedly pointed out the great similarity between the laws governing hydrogen exchange with bases and metallation with alkali-metal alkyls. All the known facts lead to the conclusion that these reactions take place *via* a stage which can be represented in the general form

$$\equiv C{-}H + B^- \rightarrow \equiv C\ldots H^{+\sigma}\ldots B^{-\sigma} \rightarrow \equiv C^- + BH. \quad (35)$$

The base attacks the hydrogen of the C–H bond and initiates protolysis. Replacement of protium by a heavier isotope of hydrogen can be expected to affect the reaction velocity if the hydrogen–carbon bond is ruptured at the rate-determining stage. Bryce-Smith *et al.*[47] measured the rate of metallation of benzene and toluene with ethylpotassium, and observed a positive isotope effect, varying with temperature, when the hydrogen of the aromatic molecule was replaced by deuterium. Gronowitz and Halvarson[48] compared the rates of metallation with butyllithium of ordinary thiophen and of thiophen labelled in the α-position with tritium, and found that protium is replaced by lithium about six times as rapidly as is tritium. The investigators in both cases suggest that the existence of an isotope effect indicates that a carbon-hydrogen bond is ruptured in the transition state as a result of attack by the carbanion part of the metallating agent on the hydrogen of the aromatic C–H bond. Further investigations[49] on orientation effects in 3-substituted thiophens make improbable the electrophilic mechanism of Morton[50] for metallation reactions.

Isotopic mass has the same effect on reaction velocity in hydrogen exchange with a base. Fluorene which has been deuterated in the methylene group and methyl 2-naphthyl ketone containing deuterium in the methyl group exchange

TABLE 4.

Catalyst	k_H/k_T
H^+	9.7
CH_3COOH	11.4
CH_3COO^-	10.2
HO^-	12.9

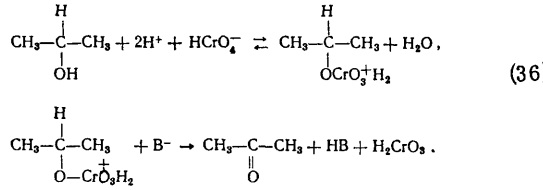
with ammonia at 25° twice as rapidly as the corresponding compounds containing tritium[51,52]. This difference in the rates of exchange can be ascribed to different activation energies for the rupture of C–D and C–T bonds in the transition state, just as with metallation reactions.

Streitwieser[53] obtained a value of $k_D/k_T = 3.0 \pm 0.3$ in an investigation of the stereochemistry of base-catalysed hydrogen exchange in the methylene group of ethylbenzene with lithium cyclohexylamide in cyclohexylamine (at 49.9°), and quoted a result of Langworthy's, who obtained values of 2.75 and 2.98 for the ratio on substituting deuterium and tritium in the methyl group of toluene. As in aromatic electrophilic substitution and hydrogen exchange with an acid, the reactivity of the reactants and the nature of the substituents and the medium must be considered for metallation and hydrogen exchange with bases. Depending on the conditions, these reactions take place by either a molecular or an ionic mechanism, and it thus becomes possible to study the effect of these conditions on the magnitude of the kinetic isotope effect. That this line of attack can give a deeper understanding of the reaction mechanism is shown by the work of Swain *et al.*[32] on the enolisation of ketones. The k_H/k_T ratio depends on the nucleophilic reagent used. It increases with increase in the basic strength of the reagent, since the proton is less firmly held in the transition state when a stronger base is involved. This relation can be seen from Table 4, which lists measurements of the kinetic isotope effect of tritium in the enolisation of 3-methyl-1-phenylbutyl phenyl ketone.

V. KINETIC ISOTOPE EFFECT OF TRITIUM IN HYDROGEN TRANSFER REACTIONS

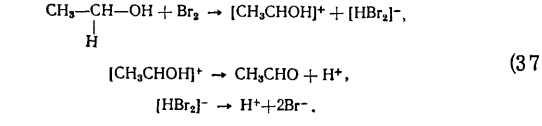
A considerable amount of work based on the kinetic isotope effect has been done on reaction mechanisms involving hydrogen transfer. In most cases the change in reaction velocity when protium is replaced by deuterium has been determined. Great attention has been paid to various reactions involving the oxidation and reduction of organic compounds, the Cannizzaro reaction, the Meerwein–Pondorf reaction, etc. Miklukhin and Rekasheva[54,55] used in particular the kinetic isotope effect of deuterium to investigate the mechanism of reactions of this type. We shall consider briefly some work in which tritium was employed.

The large kinetic isotope effect found[56] in the oxidation of 2-deuteropropan-2-ol with chromic acid and in the oxidation of benzaldehyde with chromic acid, permanganate, and other oxidants indicates that the C–H bond is ruptured in the rate-determining stage of the reaction. The magnitude of the isotope effect is found to depend on the acidity of the medium. These fundamental conclusions were confirmed and supplemented in an investigation of these and similar reactions, with partial substitution of hydrogen for tritium in the reactant molecules. According to Brown and Kaplan[8], the experimental k_T/k_H ratio found for the oxidation of propan-2-ol varies from 0.13 to 0.26 when the chromic acid concentration changes from 0.3 to 2 M. In the presence of manganous ions, which convert Cr^{IV} into Cr^{III} ions, the ratio is 0.04. Thus change in the acidity of the medium has an appreciable influence on the isotope effect. On the basis of these results, the following scheme was suggested[57,58] for this process



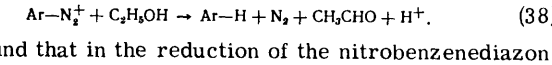
(36)

$k_H/k_T = 5$ at 37.5° has been found in the chromic acid oxidation of benzyl alcohol labelled with tritium at the α carbon atom. In the bromine oxidation of tritium-labelled ethanol an isotope effect equivalent to $k_H/k_T = 6.7$ was observed at the α carbon atom[59]. This result, like those obtained in the work mentioned above, is evidence of the occurrence of a slow stage in which a hydrogen atom is split off and added to the attacking reagent, the Br_2 molecule. This *ipso facto* casts doubt on the intermediate formation of ethyl hypobromite, which has been suggested to precede that of acetaldehyde which is the final product[60]. The following reaction scheme is claimed to be more probable[60]:



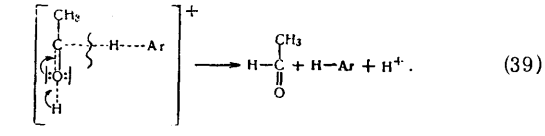
(37)

The very slight isotope effect observed when the Cannizzaro reaction is carried out with benzaldehyde labelled with either deuterium or tritium in the aldehyde group indicates that rupture of the C–H bond with transfer of a hydride ion does not occur[4]. An isotope effect was observed in the reduction of diazonium salts with alcohols[3,61] containing tritium (or protium) attached to the α carbon atom, the general scheme of this reaction being



(38)

It was found that in the reduction of the nitrobenzenediazonium ion the alcohol labelled with tritium (CH_2TOH or CH_3CHTOH) is used up at a rate about one-seventh of that with the alcohol containing no tritium. This led Melander[61] to infer a reduction mechanism similar to Dewar's for reactions of this type. In the reduction of a diazonium salt hydrogen transfer is apparently effected in a single bimolecular act, which Melander regards as an electrophilic S_E2 hydrogen substitution. The magnitude of the isotope effect indicates a rate-determining rupture of the carbon–hydrogen bond in the transition state, whose structure can be represented, if the process is ionic in character, as follows:



(39)

It is possible, however, as Miklukhin and Rekasheva[62] remark, that this reaction may occur homolytically, by a free-radical mechanism.

VI. APPLICATION OF THE KINETIC ISOTOPE EFFECT OF TRITIUM TO THE INVESTIGATION OF THE MECHANISM OF SOME OTHER REACTIONS

The kinetic isotope effect can be used to study a great variety of reactions. Apart from the work discussed in the present review, several other investigations are of great interest. Work on the kinetic isotope effect in the acid and base catalysis of ionic reactions in solution, discussed in a review by Wiberg[4], is very important.

Assarsson[63-65] has studied the kinetic isotope effect using tritium in the neutralisation of carbanions. These investigations are especially important because very many substances labelled with hydrogen isotopes are actually prepared by decomposing the corresponding Grignard compounds with water or alcohol.

Some work[67,68] has been done on the mechanism of the hydrolysis of trialkylsilanes using deuterium and tritium.

Antonovskii and Berezin[69-71] used the isotope effect substituting tritium for hydrogen in benzene and in a number of paraffins, in studies of the mechanism of the reaction of these compounds with methyl radicals in the liquid phase.

In the field of heterogeneous catalysis the kinetic isotope effect of deuterium and tritium has been used[72] to study the mechanism of the exchange between cyclohexene and water on a platinum catalyst. The kinetic isotope effect was used by Boreskov[73,74] to determine the molecularity of exchange reactions, in particular of hydrogen with deuterium and tritium on metallic catalysts.

A great deal of work using the kinetic isotope effect has been done on reactions in the gas phase. Weston[75] used this method to make an experimental test of the kinetic scheme for the occurrence of a unimolecular reaction as a function of the pressure. The isotope effect of tritium has proved useful in the study of gaseous chain reactions for determining the rate-determining stage in the photochemical reaction of hydrogen with chlorine[76] and in the branched-chain oxidation of hydrogen containing tritium under the influence of the β-rays from tritium[77].

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Tritium is widely used in reaction-mechanism studies. This review has been restricted to work in which the kinetic isotope effects of tritium and deuterium have been used in reactions involving the substitution, exchange, and transfer of hydrogen. It is clearly possible to obtain in many cases a more precise idea of the mechanism of a given reaction, especially when measurement of isotope effects is reinforced by an investigation of other aspects of the reaction. Nevertheless, several facts connected with the interpretation of the values obtained for the kinetic isotope effects have not yet received adequate explanation.

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