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EXCHANGE OF HALOGEN BONDED ON AROMATIC CORE. HETEROGENEOUS CATALYSIS—I

REACTION MECHANISM OF IODINE EXCHANGE IN *o*-IODOBENZOIC ACID

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Abstract—Reaction mechanism of halogen exchange between arylhalogenide and halogenide anion is studied in a case when the aromatic core is inactivated with respect to the S_NAr substitution by other substituents. The exchange of iodine between *o*-iodobenzoic acid and ^{131}I labelled NaI serves as a modelling reaction. The reaction was found to proceed heterogeneously on a glass surface. In the case of a rapid course of the surface reaction the reaction mechanism is more complicated and the equation derived by McKay cannot be applied for expressing the time dependence of the degree of isotopic exchange. Reaction mechanism was proposed for this reaction and compared with experimental data.

In the majority of preceding papers in which the reaction mechanism of the exchange of a halogen bonded on an aromatic core with a halogen anion was studied, the dependence of the reaction rate on component concentration was found to be of the second order (of the first order with respect to both the anion and the arylhalogenide), which corresponded to the supposed S_NAr mechanism.[1-6] In addition, the reaction rate was found to be proportional in these cases to the localization energy calculated by the help of the Hückel method of molecular orbitals, so that in those cases, when the benzene core was inactivated by a substituent suppressing the nucleophillic substitution (the localization energy was high), the reaction should not proceed with an apparent rate.[7] In contrast to this, a number of compounds such as *o*-, *m*-, *p*-iodotoluene,[8] *o*-, *p*-iodophenol,[8,9] *o*-iodobenzoic acid.[10] and *o*-iodohippuric acid were observed to exchange the halogen bonded in their molecule with halogenide anion in the solution in a reaction the rate of which is approximately zero order with respect to the anion. Vanka[12] studied the exchange of iodine in *o*-iodobenzoic acid in more detail and he found a number of anomalies in the course of this reaction (induction period, dependence of reaction order on reaction mixture composition, considerable irreproducibility of results, etc). Because is no case the formation of by-products (e.g. phenols, etc) was observed during the exchange reaction, it is improbable that the reaction should be controlled by the S_{N1} mechanism and a different explanation must be searched for. Bochkarev *et al*[13] supposed the reaction to be catalysed by trace amounts of metal salts with variable valency; light and oxygen from air may also affect the reaction; Bovington *et al*[14] found that at low iodine concentrations the exchange of iodine in 2,4-dinitroiodobenzene proceeds via heterogeneous reaction on glass.

The aim of this work was to find the reaction mechanism of reactions of this type and the exchange of iodine between *o*-iodobenzoic acid and ^{131}I labelled NaI was selected as the model reaction.

EXPERIMENTAL

Chemicals. MeOH (anhyd) and EtOH (96%) of AR purity were purified by triple distillation. NaI of AR purity was recrystallized from redistilled water. *o*-iodobenzoic acid (*o*-IBA) was prepared from anthranilic acid by means of diazotation and Sandmayer reaction and subsequent crystallization from water to constant m.p. of 162°.

Carrier-free soln of $Na^{131}I$ in 0·01 N NaOH (prepared in Nuclear Research Institute, Řež, Czechoslovakia) was used for the preparation of $Na^{131}I$ stock soln. The required amount of this soln (approximately 5 mc) was pipetted into an evaporation dish, neutralized with several drops of dil HCl, and small amounts of NaI and Na_2SO_3 (in order for the final concentration in the stock soln to be approx 1×10^{-5} M) were added. The soln was evaporated to dryness on a water bath and the residue was dissolved in a solvent identical with that used for the exchange reaction.

The remaining chemicals were of AR purity and were used without purification.

Glass powder was prepared by grinding glass tubes (glass Simax) in a porcelain mortar; two fractions with the particle sizes of $2{\cdot}5 \times 10^{-2}$ cm (I) and 5×10^{-3} cm (II) and surface areas of 100 cm²/g and 250 cm²/g, resp., were separated by sieve analysis. The powder was boiled before use for 5 hr in a solvent identical with that which was used for the exchange reaction.

Experimental procedure. The reaction mixture of 10 ml was heated in a drop-shaped flask (25 ml) in a thermostat (with the accuracy of ±0·1°) under reflux. In all cases, with the exception of the experiments of information character, the mixture was well stirred with a glass stirrer. The temp was adjusted before the beginning of the exchange reaction in two ways: (a) constant temp of the mixture without active Na^{131}I was adjusted during simultaneous mixing for 30 min after which the required amount of Na^{131}I stock soln was added and the time was measured from this point; (b) the temp of the mixture, without both active and inactive NaI, was adjusted at simultaneous mixing for 30 min in one reaction vessel while the temp of the mixture of both active and inactive NaI was adjusted for an identical time period in another vessel. In time $t = 0$, the corresponding amount of NaI + Na^{131}I soln was transferred into the vessel. The stock soln of *o*-IBA, NaI, Na^{131}I and the glass powder were identical in one series of experiments, so as to ensure the best possible reproducibility of experimental conditions. Samples from the reaction were taken by a polyethylene capillary and transferred to the chromatogram start. Whatman No. 4 paper was used and descending chromatography with the system benzene–acetic acid–water 2:2:1 (organic phase) in which R_F of iodine and *o*-IBA equalled 0·0 and 1·0, resp. After drying the chromatogram, it was cross cut at R_F of approximately 0·2 and the activity of both parts measured in a well-type scintillation crystal.

Evaluation of results. The exchange degree F was calculated from the relation

$$F = \frac{\text{activity in } o\text{-IBA in time } t}{\text{total activity of the system}} \cdot \frac{A + B}{B}$$

where A and B are the concentrations of NaI and *o*-IBA (mole . l^{-1}), resp, in the mixture and the log (1–F) dependence was plotted against time.

RESULTS AND DISCUSSION

Preliminary experiments were carried out with a mixture of the composition $A = B = 1 \times 10^{-2}$ mole . l^{-1}, the amount of the stock solution of Na^{131}I was 0·05 – 0·2 ml (depending on its specific activity). These experiments showed that light, the presence or absence of oxygen from air, as well as the presence of small amounts of salts of bivalent and trivalent iron or univalent and bivalent copper did not affect the exchange rate. On the other hand the exchange reaction rate considerably increased when mixing the reaction mixture during the reaction and along with it, the reproducibility of the results was considerably better. These facts indicated the reaction to be controlled by the heterogeneous mechanism on reaction vessel surface and further experiments were aimed at verifying this hypothesis and at determining the reaction mechanism in detail.

The first studied dependence was that of the exchange rate on surface area. Surface area of glass in contact with the reaction mixture was varied by means of adding various amounts of glass powder into the mixture. Fig 1 (points marked ○) shows the dependence of $1/t_{1/2}$ (min^{-1}) on glass powder (I) amount in grams in 10 ml of the mixture ($t_{1/2}$ is the reaction half-time, i.e. the time in which $F = 0·5$; $1/t_{1/2}$ is therefore proportional to the reaction rate). Reaction conditions: $A = B = 1 \times 10^{-2}$ mole . l^{-1}, solvent – 50 volume % of aqueous methanol, 50°, temperature adjusted according to procedure (a), i.e. the mixture was chemically equilibrated before adding Na^{131}I (see Exp.). Under these conditions, the log (1–F)-to-t dependences were linear. When the reaction components were thermostated separately and mixed only at the beginning of the exchange reaction (the temperature of the solution was adjusted according to b, see Experimental), the course of the log (1–F)-to-t dependence presented in Fig 2, was not linear. Reaction conditions: $A = B = 1 \times 10^{-2}$ mole . l^{-1}, glass powder (II), solvent – 50 volume % aqueous ethanol, 80°. If $t_{1/2}$ is read off from the slope of curve at $t = 0$ and $1/t_{1/2}$ is plotted against the amount of glass powder, linear dependence is again obtained (Fig 1, points marked □).

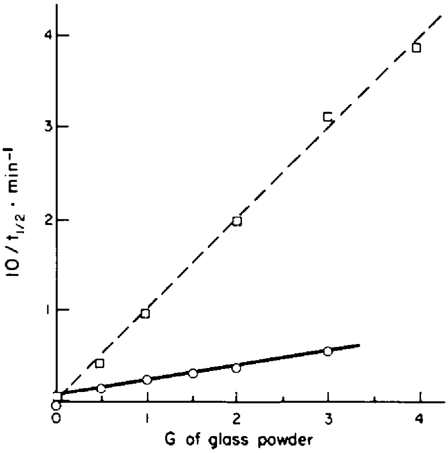


Fig 1. Dependence of $1/t_{1/2}$ (min^{-1}) on the amount of glass powder in reaction mixture; ○ glass powder (I), □ glass powder (II).

The dependence of the exchange rate on NaI concentration was studied in the next stage. Fig 3 demonstrates the log R-to-log A dependence, where R is the exchange reaction rate in mole . l^{-1} . sec^{-1}, $A = 1 \times 10^{-5}$ through 5×10^{-2} mole . l^{-1}, solvent – 70 volume % of aqueous methanol, 60°, 1·5 g of glass powder (I), constant temperature maintained according to (a). At $A \geq 1 \times 10^{-3}$ mole . l^{-1} the log (1–F)-to-t dependences were linear, at lower concentrations of A they had a shape shown in Fig 4b. The reaction rate was in these cases determined from the linear part of the curve at $t > 20$ min. (the method of the calculation of rate R is discussed below).

The dependence of the logarithm of exchange rate (log R) on the logarithm of *o*-IBA concentration was linear with the slope of 0·724. At *o*-IBA

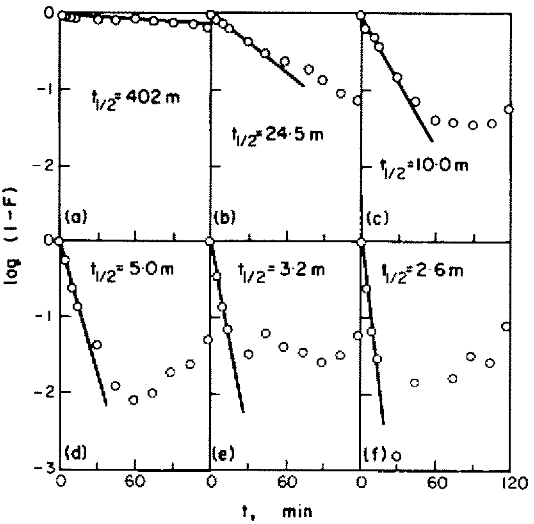


Fig 2. Character of log (1–F)-to-t dependence for various amounts of glass powder (II) in reaction mixture (the temperature of the single reaction components was adjusted separately); (a) 0 g, (b) 0·5 g, (c) 1 g, (d) 2 g, (e) 3g, and (f) 4 g.

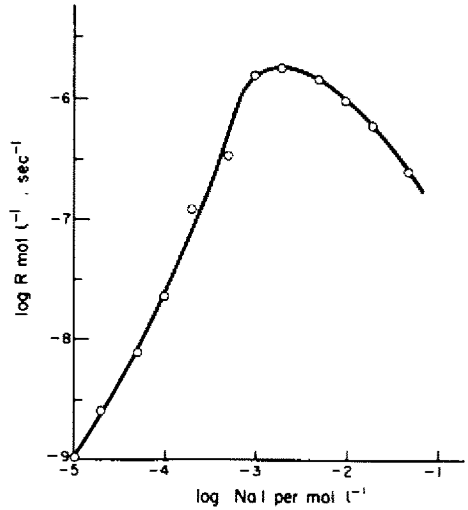


Fig 3. Dependence of log R on log (NaI); *o*-IBA concentration equalled 1×10^{-2} mole . l^{-1}.

concentrations exceeding 1×10^{-3} mole . l^{-1} the log (1–F)-to-t dependence was linear, at lower concentrations it had the shape similar to that presented in Fig 4b.

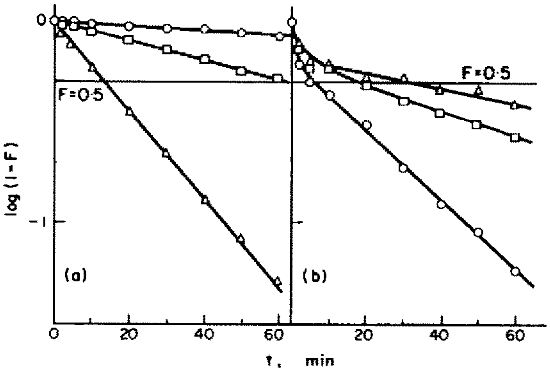


Fig 4. Character of log (l–F)-to-time dependences at various NaI concentrations (mole . l^{-1});
(a) ○ 5×10^{-2}, □ 1×10^{-2}, △ 1×10^{-3}
(b) ○ 5×10^{-4}, □ 1×10^{-4}, △ 2×10^{-5}.

Table 1. Dependence of exchange rate on NaCl concentration in reaction mixture

NaCl mole . l^{-1}	$t_{1/2}$ min.	r_1 mole . l^{-1} . sec^{-1}
0	83·5	$1{\cdot}383 \times 10^{-8}$
1×10^{-3}	85·5	$1{\cdot}351 \times 10^{-6}$
1×10^{-2}	133	$8{\cdot}684 \times 10^{-7}$
$2{\cdot}5 \times 10^{-2}$	165	$7{\cdot}000 \times 10^{-7}$
$7{\cdot}7 \times 10^{-3}$	450	$2{\cdot}566 \times 10^{-7}$

The dependence of the exchange rate on NaCl concentration in the mixture was studied in the next stage. Results of experiments with various concentrations of NaCl are given in Table 1. Reaction conditions: A = B = 1×10^{-2} mole . l^{-1}, solvent – 70 volume % of aqueous methanol, NaCl concentration between 0 and $7{\cdot}7 \times 10^{-2}$ mole . l^{-1}, 60°, 1·5 g of glass powder (I), temperature adjusted according to (a). The log (1–F)-to-t dependences are linear.

The dependence of the exchange rate on the degree of *o*-IBA dissociation was also studied. Values of $t_{1/2}$ (and exchange rates calculated from them) read off from the slope of the log (1–F)-to-t dependence at t = 0 and at different degrees of *o*-IBA dissociation are collected in Table 2. The different dissociation degrees were adjusted by means of adding the solution of potassium ethanolate in absolute ethanol to the mixture in order for its molar concentration to equal 0, 5, 10, 20, and 80% of the molar concentration of *o*-IBA. Reaction conditions: A = B = 1×10^{-2} mole . l^{-1}, the corresponding amount of EtOH solution in absolute EtOH, solvent – absolute EtOH, 75°, 3·0 g of glass powder (I), constant temperature adjusted according to (a).

Table 3 shows the dependence of the reaction rate on temperature. The log (1–F)-to-t dependences were linear at 50, 55, 60, and 65°, at 70° the exchange rate decreased at longer reaction times (similarly to Fig 4b). Reaction conditions: A = B = 1×10^{-2} mole . l^{-1}, solvent – 70 volume % aqueous methanol, temperature 50, 55, 60, 65,

Table 2. Dependence of exchange rate on dissociation degree of *o*-IBA

EtOK mole . l^{-1}	$t_{1/2}$ min.	r_1 mole . l^{-1} . sec^{-1}
0	260	$4{\cdot}44 \times 10^{-7}$
5×10^{-4}	180	$6{\cdot}42 \times 10^{-7}$
1×10^{-3}	112	$1{\cdot}03 \times 10^{-6}$
2×10^{-3}	62	$1{\cdot}86 \times 10^{-6}$
8×10^{-3}	30	$3{\cdot}85 \times 10^{-6}$

Table 3. Dependence of exchange rate on temperature

Temperature °C	$t_{1/2}$ min.	r_1 mole . l^{-1} . sec^{-1}
50	215	$5{\cdot}372 \times 10^{-7}$
55	156	$7{\cdot}404 \times 10^{-7}$
60	110	$1{\cdot}050 \times 10^{-6}$
65	86·5	$1{\cdot}335 \times 10^{-6}$
70	70·0[a]	$1{\cdot}650 \times 10^{-6}$

[a] Tangent line at t = 0.

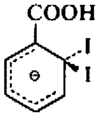
and 70°, 1·5 g of glass powder (I), constant temp adjusted according to (a).

The presented experimental results show that the heterogeneous mechanism actually controls the exchange. The non-linear log (1–F)-to-t dependence observed in some cases indicates, however, that the reaction course is more complicated. This phenomenon was observed experimentally in those cases, when for any reason the reaction is accelerated (higher temperature, larger surface area, higher degree of *o*-IBA dissociation), which can indicate the accumulation of an unstable intermediate reaction product in the mixture. The possibility of the existence of side reactions was eliminated by means of isolating from the mixture after finishing the exchange reaction the organic phase and by means of a mixed m.p. with *o*-IBA that had not been used their identity was proved. On the basis of these results and of the usual conception of the course of heterogeneously catalysed reactions,[15] the following reaction mechanism was proposed:

$$\begin{tikzcd}
(I^-) + (IB) \arrow[d, shift left, "r_5"] & (IB I^-) \text{ (homogeneous phase) (I)} \arrow[l, "r_3"'] \arrow[d, shift left, "r_9"] \\
(I^-)_A + (IB)_A \arrow[u, shift left, "r_4"] \arrow[r, shift left, "r_1"] & (IBI^-)_A \text{ (catalyst surface)} \arrow[l, shift left, "r_2"] \arrow[u, shift left, "r_8"]
\end{tikzcd}$$

(with r_6 and r_7 on the arrows between (IB) and $(IB)_A$)

where r_i is the rate of i-th reaction, (I^-), (IB), and (IBI^-) are the concentrations in mole . l^{-1} of iodide anions, *o*-IBA and of the transition π-complex of the Meisenheimer type (2) in the solution, resp, and $(I^-)_A$, $(IB)_A$, and $(IBI^-)_A$ are the respective concentrations of these components in mole . g^{-1} of the catalyst on its surface.



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The rates of surface reactions r_1 and r_2 may be expressed by Eqs[15] (1) and (2):

$$r_1 = Gk_1 \frac{s}{L} (I^-)_A (IB)_A \tag{1}$$

$$r_2 = Gk_2 \frac{s}{L} p(IBI^-)_A \tag{2}$$

where G is the number of grams of the catalyst in unit volume of the mixture, L is the amount of active centres per 1 g of the catalyst (mole . g^{-1}), each centre has s adjacent centres in identical distances, p is the concentration of non-occupied absorption centres per 1 g of the catalyst (mole . g^{-1}), and k_1 and k_2 are the respective rate constants. The rate of the decomposition of the transition complex in the homogeneous phase is expressed by the equation:

$$r_3 = k_3(IBI^-). \tag{3}$$

The rate of the reaction reverse with respect to (3), i.e. the rate of the formation of the transition complex in the homogeneous phase is evidently immeasurable as indicated from the fact that the dependence of the reaction rate on surface area (Fig 1) passes through the origin. $r_i(i = 4$ through $9)$ are the rates of adsorption and desorption of the respective components.

The proposed mechanism was verified by means of comparing the log (l–F)-to-t dependence derived theoretically on the basis of this mechanism with experimental results. Eq (4) is the resulting relation (the derivation see in the Appendix):

$$\begin{aligned}(l\text{–}F) = &\frac{1}{D}\left\{\frac{a_1 H(A+B)}{2B} + b_1\right\} e^{b_2 t} \\ &- \frac{1}{D}\left\{\frac{a_1 H(A+B)}{2B} + b_2\right\} e^{b_1 t}\end{aligned} \tag{4}$$

where

$$b_{1,2} = \tfrac{1}{2}\{-a_1(E+H) - (a_2+a_3) \pm D\} \tag{4a}$$

$$D = \{(a_2+a_3)^2 + a_1^2(A-B)^2\}^{1/2} \tag{4b}$$

$$\begin{aligned} a_1 &= Gk_1 \frac{s}{L} p^2 K_I K_{IB} \\ a_2 &= Gk_2 \frac{s}{L} p^2 K_{IBI} \\ a_3 &= k_3. \end{aligned} \tag{4c}$$

In all cases, when the reaction rate r_1 is for any reason small, the concentration of (IBI^-) will be also small and $A = E$, $B = H$. The rate constants of the decomposition of the transition complex may be supposed to be considerably higher than those of its formation, i.e. $(a_2+a_3) \gg a_1$, and Eq (4b) is transformed to the form $D = (a_2+a_3)$. After substituting into Eq (4) and rearranging we obtain

$$\log(1-F) = -\frac{a_1(A+B)}{2\times 2{\cdot}303}t \qquad (5)$$

which is the equation derived by McKay[16]

$$\log(1-F) = -\frac{R(A+B)}{2{\cdot}303\,AB}t$$

for the time dependence of (l–F), and where the rate R has the form

$$R = \frac{a_1AB}{2} = \frac{Gk_1sLK_IK_{IB}AB}{2\left(1+K_IA+K_{IB}B+\sum K_iX_i\right)^2} \qquad (6)$$

where expression

$$p = \frac{L}{1+K_IA+K_{IB}B+\sum\limits_i K_iX_i}$$

was substituted for p (concentration of free adsorption centres).

K_i, X_i are the equilibrium adsorption constants or the concentrations of inert components of the mixture (solvent, inert electrolyte). McKay's equation may be therefore used when the process controlling the total reaction rate is r_1 and the concentration of the intermediate product may be neglected in comparison with the concentrations of the initial components. The log (l–F)-to-t dependence is linear in this case and the rate R can be calculated from the reaction half-time.

Linear dependence of R on the amount of glass powder in the mixture G (i.e. on surface area) follows from Eq (6) (Fig 1). It follows also from this equation that the concentration of free adsorption sites, and in this way also the reaction rate, decrease with the addition of the electrolyte into the mixture (Table 1). This equation explains also the dependence of R on NaI concentration (Fig 3) for concentrations $A \geq 1\times10^{-3}$ mole . l^{-1}. At lower concentrations of iodide the condition $A \doteq E$ is no longer fulfilled and the log (l–F)-to-t dependence has the character of the sum of two exponential dependences (Fig 4b) as it follows from Eq (4). Values of R for $A < 1\times10^{-3}$ mole . l^{-1} were calculated from the slope of the tangent line of the log (l–F)-to-t dependence at longer time periods, for which relation

$$b_1 = -\frac{a_1(E+B)}{2\times 2{\cdot}303}$$

follows from Eq (4). In this case, the initial concentration A was taken instead of the unknown value of E when calculating a_1. This inaccuracy might become evident in the value of the slope of the log R-to-log A dependence at lower concentrations when it equalled approximately 1·5 instead of the theoretical value of 1·00. Quite similar is the situation with the dependence of R on *o*-IBA concentration. Owing to the low dissociation of *o*-IBA its adsorption constant K_{IB} is probably low and for this reason, the log R-to-log B dependence is linear in the studied concentration range of B between 2×10^{-4} and 5×10^{-2} mole . l^{-1}. Its dissociation decreases with the increasing concentration of *o*-IBA and in this way also its value of K_{IB} so that the resulting slope equals 0·724 instead of 1·00 as it would follow from Eq (6). If the dissociation degree of *o*-IBA is elevated (e.g. by means of adding alkalies into the mixture), K_{IB} and therefore r_1 increases too, the concentration of the intermediate product also increases and the log (1–F)-to-t dependences for additions into the mixture of EtOK equal to 10% and more of the content of *o*-IBA possess the shape similar to that presented in Fig 4b. The relation for the slope of these dependences at $t = 0$ may be obtained by means of differentiating Eq. (4):

$$\left[\frac{d\log(1-F)}{dt}\right]_{t=0} = -\frac{a_1(A+B)}{2\times 2{\cdot}303}\left\{1-\frac{(IBI^-)}{B}\right\}. \qquad (7)$$

If the second term in the brackets is neglected compared with unity, rate r_1 can be determined approximately from the slope at $t = 0$ (Table 2).

The system was supposed in all above-mentioned cases to be in chemical equilibrium before adding radioactive iodide (method of temperature adjusting according to (a), see Experimental). If the temperature of the separate reaction components was adjusted (temperature adjusting according to (b)) and if the formation of the intermediate product starts simultaneously with the exchange reaction, the equality (8A) is no longer valid and Eqs (6A) and (7A) (see Appendix) change into a system of nonlinear equations which have no general solution. Figure 2 shows that the character of the log (1–F)-to-t dependence also changes in this case. A minimum appears on the curves that deepens with the increasing surface area, most likely due to the increasing concentration of the intermediate product and decreasing concentration of the initial components. The derivative of log (l–F) with respect to time at $t = 0$ has under these conditions the form of Eq (7) without the second term in the brackets (the concentration of the intermediate products equals zero at $t = 0$) and reaction half-time may be determined from it at $t = 0$.

The dependence of the reciprocal value of this half-time on glass powder surface area is given in Fig 1, points marked □.

Activation energy of 12·9 kcal/mole was determined from the temperature dependence of rate r_1. It is a mean value, because the log r_1-to-1/T dependence is not strictly linear, which might result from the fact that not only the reaction constant k_1 in the constant a_1 (Eq (4c)) is temperature dependent but so also are all adsorption constants.

It may be concluded that the isotopic exchange of iodine between *o*-IBA and iodide anions is controlled by the heterogeneous reaction on glass surface. In the case of a faster course of the surface reaction, the mechanism is more complicated and the equation derived by McKay cannot be used for expressing the dependence of the degree of isotopic exchange on time. The proposed mechanism agrees with experimental data.

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APPENDIX

On the basis of the proposed mechanism (I) a system of corresponding differential equations may be derived expressing the time dependence of the reaction components concentrations. Because this system is rather complicated to be able to be solved in general, certain simplifications must be introduced.

If the rate of adsorption and desorption are supposed to be considerably higher than the rates of reactions (1), (2), and (3), the adsorption proceeds under practically equilibrium conditions and it holds:

$$(I^-)_A = pK_I(I^-) \qquad (1A)$$

$$(IB)_A = pK_{IB}(IB) \qquad (2A)$$

$$(IBI^-)_A = pK_{IBI}(IBI^-)_A \qquad (3A)$$

where K_I, K_{IB}, and K_{IBI} are the respective equilibrium adsorption constants and Eqs (1) and (2) may be rewritten into the form

$$r_1 = Gk_1p^2K_IK_{IB}(I^-)(IB)\frac{S}{L} \qquad (4A)$$

$$r_2 = Gk_2\frac{S}{L}p^2K_{IBI}(IBI^-). \qquad (5A)$$

Because the catalyst is a compact (nonporous) substance and the mixture was intensively stirred during the reaction, the effect of the diffusion of the reaction components to the surface may be neglected. If we suppose that $G(I^-)_A \ll (I^-)$, $G(IB)_A \ll (IB)$ and $G(IBI^-)_A \ll (IBI^-)$, we obtain from the stoichiometric reactions

$$(I^-) = A - (IBI^-) = E$$

$$(IB) = B - (IBI^-) = H$$

where A and B are the initial concentrations of iodide and *o*-IBA, resp.

Now the relations for the (l–F)-to-t dependence may be derived. It holds

$$c_I^0 = (I^-)^+ + (IB)^+ + (IBI^-)^+$$

where $(I^-)^+$, $(IB)^+$, and $(IBI^-)^+$ are the concentrations of the respective components containing one radioactive atom in the molecule (mole . l^{-1}), and c_I^0 is the total concentration of radioactive atoms in the solution. Supposing the concentration of radioactive atoms to be considerably lower than that of the nonradioactive ones it holds $(I^+BI^+) \ll (IBI)^+$ and the concentration of twice labelled complex may be neglected. On the basis of the supposition that the rate of radioactive atom transition from the molecule of one component to the molecule of another one equals the product of the rate of the respective chemical reaction r and of the difference in the specific activities of these compounds[16] and on the basis of the preceding considerations we obtain:

$$\frac{d(IB)^+}{dt} = -r_1S_{IB} + (r_2 + r_3)S_{IBI} + [r_1 - (r_2 + r_3)]S_{IB}S_{IBI} \qquad (6A)$$

$$\frac{d(IBI^-)^+}{dt} = r_1S_I + r_1S_{IB} - 2(r_2 + r_3)S_{IBI} - [r_1 - (r_2 + r_3)](S_IS_{IBI} + S_{IB}S_{IBI}) \qquad (7A)$$

where S are the specific activities of the components, defined as:

$$S_I = \frac{(I^-)^+}{E};\ S_{IB} = \frac{(IB)^+}{H};\ S_{IBI} = \frac{(IBI^-)^+}{2(IBI^-)}.$$

Supposing the sytem to be in time $t = 0$ (i.e. in the moment when radioactive I^- was added into the system) in chemical equilibrium, it holds

$$r_1 = r_2 + r_3 \tag{8A}$$

and the last terms in Eqs (6A) and (7A) disappear. Because the (IBI^-) complex is very unstable, it rapidly decomposes to *o*-IBA and I^- during taking the sample from the mixture and radioactive iodine passes uniformly into both components. The degree of exchange F may be therefore expressed by the relation:

$$F = \frac{(IB)^+ + \frac{1}{2}(IBI)^+}{c_1^0} \cdot \frac{E + H + 2(IBI^-)}{H + (IBI^-)}$$

$$= \frac{(IB)^+ + \frac{1}{2}(IBI^-)^+}{c_1^0} \cdot \frac{A + B}{B}. \tag{9A}$$

Solving Eqs (6A) and (7A) and taking into consideration Eq (9A) we obtain the resulting relation (4).