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An Examination of the Reliability of Methods of Analyzing the Experimental Data from Exchange Reactions of Molecules with Nonequivalent Hydrogen Atoms

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Methods of analyzing the data from catalytic exchange reactions of molecules in which different groups of hydrogen atoms exchange at different rates have been tested using computer-generated isotopic distributions. The method of determining rates of exchange from such reactions at constant temperature, proposed by Harper, Siegel, and Kemball, is found to be satisfactory provided that the ratio of the rate constants for two groups of exchangeable hydrogen atoms is greater than about 5.

On the other hand, the derivation of rate constants and Arrhenius parameters from data obtained by temperature-programmed experiments can only be considered reliable when the ratio of rate constants for the different groups of atoms is greater than about 20.

INTRODUCTION

In exchange reactions of hydrocarbons and other substances with deuterium, the various hydrogen atoms in the molecule frequently react at different rates, e.g., for the alkylbenzenes, a marked difference is observed in the reactivity of the side group and of the ring hydrogen atoms over a wide range of catalysts (*1*). It is desirable that the maximum amount of information about the rates of exchange of the different types of hydrogen atoms should be obtained from experimental data for such systems, but the selection of a reliable method of analyzing the data may be difficult.

The problem has been solved for the case of molecules having hydrogen atoms in two groups, both exchanging in a stepwise fashion but at different rates (*2*). Bolder, Dallinga, and Kloosterziel (*3*) gave a general treatment for multiple exchange but limited it to molecules with a single group of exchangeable hydrogen atoms. They also considered a method for molecules with nonequivalent hydrogen atoms involved in multiple exchange but subject to two conditions: Firstly, the reaction starts with undeuterated hydrocarbon molecules and, secondly, the fraction of deuterium in the deuterating agent remains constant. This latter condition implies that their analysis cannot be applied to experimental situations, commonly found in heterogeneous catalysis, in which the dilution of the deuterium by hydrogen from the reactant hydrocarbon cannot be neglected.

Approximate methods of obtaining rate constants from experimental data were proposed by Crawford and Kemball (*4*) and subsequently improved by Harper, Siegel, and Kemball (*5*). The latter method which we shall call the HSK method can be applied to cases with two or more groups of hydrogen atoms reacting at different rates by either stepwise or multiple mechanisms. Intuitively, one would expect that the HSK method gives reliable results in the limit of one group exchanging very much faster than the next group, but some doubt exists as to how well the method works when the rates of exchange of different groups are comparable. The first objective of the present research was to attempt to determine the conditions under which the HSK method is reliable.

Temperature-programmed catalysis has

been used as a technique for following the exchange of groups of nonequivalent hydrogen atoms (*6*), and the analysis of results involves an extension of the HSK method. The technique provides information from a single experiment which could only be obtained from several experiments carried out in a conventional manner at constant temperature. Arrhenius parameters as well as relative rates of reaction of the different groups of hydrogen atoms are obtained, but the limits of the reliability of the approach have not been established. Investigation of this problem is the second objective of the present paper.

The method of investigating both problems involved the use of equations derived by Dallinga *et al.* (*2*) to compute distributions of isotopic species for exchange reactions for a molecule with two groups of hydrogen atoms reacting in a stepwise manner. These computed distributions were taken as "experimental data," analyzed by the HSK method and its extension for temperature-programmed catalysis, and the calculated rates were then compared with the actual rates used to generate the "experimental data." In this way, information about the useful limits of the HSK method was obtained.

NOMENCLATURE

D_A, D_B	Mean deuterium content in groups of hydrogen atoms, A and B, respectively. [These correspond to D and Δ in Ref. (*2*).]
d_i	Percentage of isotopic species containing i deuterium atoms
E	Activation energy for exchange of hydrogen atoms
k	Total rate constant for exchange of hydrocarbon
k_A	Rate constant for exchange of hydrogen atoms in group A. (Similar definitions for k_B, k_L, k_M.)
k_0	Initial value of k in temperature-programming experiment
$\bar{k}$, $\bar{k}_A$, etc.	Mean values of k, k_A, etc., over time intervals in temperature-programming experiment
N_A, N_B	Number of hydrogen atoms in group A and group B, respectively
T	Temperature of reaction
T_0	Initial temperature in temperature-programming experiment
t_c	Computer time scale
t_l	Laboratory time scale
ϕ_A, ϕ_B	Measure of extent of deuteration in group A and group B, respectively
ϕ_{A_∞}, ϕ_{B_∞}	Equilibrium values of ϕ_A and ϕ_B
ϕ	Measure of extent of deuteration in hydrocarbon molecule

DERIVATION OF THE ISOTOPIC DISTRIBUTIONS

The treatment set out by Dallinga *et al.* (*2*) applies to any molecule in which hydrogen atoms can be subdivided into two groups, A and B, the latter reacting more slowly but with the exchange of both groups occurring by a stepwise process. Their theory was adapted to enable us to calculate the distribution of products during an exchange reaction.

Expressions for the variation with time of D_A and D_B, the deuterium content in group A and group B hydrogens, respectively, can be found from Eqs. (20) and (21) of Ref. (*2*). These expressions involve k_A and k_B, the rate constants for the exchange of groups A and B, respectively, the mole fraction of the reacting molecule in the total system, and the initial fraction of deuterium in the labeling compound. Thus, if the experimental conditions, i.e., the reaction mixture and the rate constants for exchange in groups A and B, are specified, D_A and D_B can be calculated for a series of values of time. Then, using the binomial expressions which apply for stepwise exchange, the distribution of isotopic species in the two groups can be derived and, on combination of the results for the two groups, an isotopic distribution for the molecule as a whole can be obtained.

Many of the calculations are repetitive using the same relationship several times.

A computer program was written to calculate the distributions. Facilities were incorporated in this program to specify N_A and N_B, the rate constants k_A and k_B, and the reaction mixture. Most calculations were carried out with $N_A = N_B = 4$, corresponding to a molecule such as naphthalene with eight exchangeable hydrogen atoms in two groups of four. In this way, sets of distributions of products at specified times were generated to be used as "experimental" distributions for which the kinetic and other experimental details were known.

CALCULATION OF RATE CONSTANTS FROM ISOTOPIC DISTRIBUTIONS

The HSK (*5*) method of obtaining rate constants from experimental distributions of isotopic species has been described elsewhere. With the exception of using k for the total rate constant rather than k_ϕ, we follow the same nomenclature.

To obtain the slower rate constant, k_B, it is assumed that the second group of hydrogen atoms exchanges much more slowly than the first group, group A. It was one of the aims of this work to investigate the lower limits of k_A/k_B for the HSK method to work satisfactorily. To obtain linear plots when deriving rate constants, correct values for ϕ_∞ must be chosen. The choice of ϕ_{B_∞} on similar lines to that described in (*5*) proved to be satisfactory, while the choice of ϕ_{A_∞} will be discussed in the section with the results.

TEMPERATURE PROGRAMMING

Temperature-programmed catalysis is used as a rapid means of comparing the rates of exchange of different kinds of hydrogen atoms in a molecule when the ratio of the rates is so great that it is impossible to choose a single reaction temperature at which both rates can be observed accurately and conveniently. The usual method is to increase temperature linearly with time so that reaction of both groups of hydrogen atoms can be followed in a single experiment. The distributions of products are obtained at equal intervals of time and analyzed by a procedure based on the HSK method (*6*).

In order to generate suitable data for studying this technique, distributions must be calculated which correctly reflect the increase in the reaction rate as the temperature increases. We have assumed that the rate constants k_A and k_B will obey the Arrhenius equation and, for simplicity, that both groups have the same activation energy, E.

The computer program was capable of calculating distributions of products at various times in the exchange reaction but with specified rate constants; it had no facility to deal with a changing rate constant. This problem was solved by defining an expanded time scale, t_c, computer time, related to laboratory time by the equation

$$\frac{dt_c}{dt_l} = \frac{k}{k_0}, \qquad (1)$$

where k_0 is the rate constant at T_0, the initial temperature, and k is the rate constant at temperature T and laboratory time t_l. The temperature was assumed to increase linearly with time. In this way the extent of the reaction for a system which had reacted under laboratory conditions for a time t_l during which the rate constant was increasing with temperature would be equivalent to that calculated for a reaction with a fixed rate constant, k_0, for time t_c. Integration of Eq. (1) gives the values of t_c which correspond to the selected values of t_l for which distributions are required. Once a list of the required values of t_c had been obtained, product distributions were calculated as before.

RESULTS AND DISCUSSION

Constant Temperature

Distributions of products were calculated at various time intervals for an arbitrary mixture of 22.6 parts of deuterium to 1 part of hydrocarbon and for values of the ratio k_A/k_B of 100, 20, 10, 5, and 1. These were then used as "experimental data."

The analysis of the results of an actual experiment requires, firstly, the recognition that not all the hydrogen atoms are exchanging at the same rate and, secondly, the determination of how many hydrogen atoms are in each group. Figures 1 and 2 show

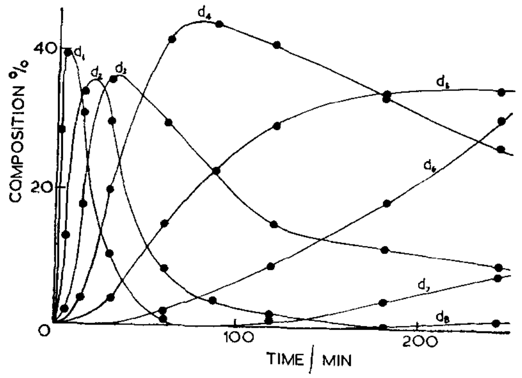

FIG. 1. Calculated isotopic distributions during reaction with k_B = 0.6 D atoms/100 molecules min^{-1} and k_A/k_B = 20.

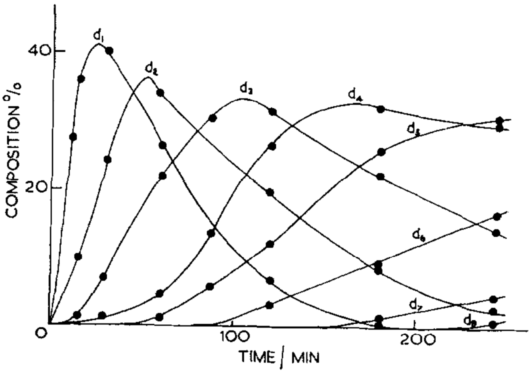

FIG. 2. Calculated isotopic distributions during reaction with k_B as for Fig. 1, but k_A/k_B = 5.

distributions of products during reaction for values of k_A/k_B of 20 and 5, respectively. The fact that four hydrogen atoms were replaced more rapidly than the second four is clear in Fig. 1 but obscured in Fig. 2.

Another method of distinguishing nonequivalent groups in a stepwise exchange is to compare product distributions with calculated binomial distributions for the same value of ϕ. The results in Table 1 show that the experimental distributions have more d_3 and d_4 species and less d_5 and d_6 species than the corresponding binomial distributions. This test works well for $k_A/k_B = 20$ or 10 and gives some indication of the division of the atoms into groups even with the ratio of 5. This test only works well at the appropriate stage of the reaction; at the beginning the distributions will be accurately binomial, but discrepancies will appear when the slower group are starting to exchange and they disappear again as equilibrium is approached. An appropriate stage to make the comparison is when the binomial distribution shows about 10% of the isotopic product with one more deuterium atom than the number of hydrogen atoms in the rapidly exchanged group, i.e., d_5 in our case.

The rate constants obtained by the HSK method are compared in Table 2 with the actual values used to generate the "experimental data." The choices of ϕ_{A_∞} and ϕ_{B_∞} are important in estimating the rate constants, and the procedure for obtaining an adequate value of ϕ_{B_∞} has been described (*5*). If ϕ_{A_∞} is correctly chosen, a linear plot should be obtained for $\log(\phi_{A_\infty} - \phi_A)$ vs time, and the derivation of the rate constant from the gradient presents no problem. Curvature of the ϕ plot convex to the line axis implies that the reaction is slowing down and that the equilibrium value of ϕ_A has been

TABLE 1
COMPARISON OF PRODUCT DISTRIBUTIONS WITH BINOMIAL DISTRIBUTIONS FOR DIFFERENT VALUES OF k_A/k_B

k_A/k_B	ϕ	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
20	319.0	0.4	4.5	18.9	37.0	31.2	7.3	0.7	0.0	0.0
(Binomial)	319.0	1.7	9.0	21.0	27.9	23.1	12.3	4.2	0.8	0.1
10	312.9	0.7	6.3	21.3	34.6	26.9	8.8	1.4	0.1	0.0
(Binomial)	312.9	1.9	9.7	21.8	28.0	22.5	11.6	3.7	0.7	0.1
5	299.5	1.5	9.3	24.0	31.7	22.7	8.8	1.8	0.2	0.0
(Binomial)	299.5	2.3	11.2	23.5	28.2	21.1	10.1	3.0	0.5	0.0

TABLE 2
Comparison of Estimated[a] and Chosen Rate Constants

k_A/k_B		k		k_B		
Chosen	Est.	Chosen	Est.	Chosen	Est.	ϕ_{A_∞}
		(D atoms/100 molecules min^{-1})				
20	21.5	14.0	14.1	$0.\dot{6}$	0.62	370
10	11.3	$7.\dot{3}$	7.38	$0.\dot{6}$	0.60	380
5	5.8	4.00	4.07	$0.\dot{6}$	0.60	400
1	4.4	$1.\dot{3}$	1.56	$0.\dot{6}$	0.29	400

[a] Rate constants calculated to ±3 in the third significant figure.

overestimated. The reverse behavior indicates that ϕ_{A_∞} has been underestimated.

Fortunately, the range of possible values for ϕ_{A_∞} was limited. If it was assumed that only four hydrogen atoms were reacting and that the remaining four were inert, the calculated value of ϕ_{A_∞} is 367 for the reaction mixture used. If the corresponding procedure to that for estimating ϕ_{B_∞} was employed, $\phi_{A_\infty} = 400$, which is the maximum possible value of ϕ_A. The ϕ plots for ϕ_A are shown in Fig. 3, and the selected values of ϕ_{A_∞} are given in Table 2. It is not surprising that a lower value of ϕ_{A_∞} was more satisfactory for the case of $k_A/k_B = 20$ and that the higher values were better for the case where there was less difference between the rates of reaction of the two groups of atoms.

Figure 4 shows the plots for ϕ_B in the appropriate form to determine the rate of exchange of the slower group of hydrogen atoms. It was not possible to evaluate ϕ_B satisfactorily for distributions with less than 10% of the total hydrocarbon present as d_5 or higher species. Each of these plots showed similar behavior and fell into three sections. The first part was curved and the curvature was more pronounced and lasted longer for the lower values of k_A/k_B. The second sections were reasonably linear, particularly for the higher values of k_A/k_B, and were used to estimate the rates given in Table 2. In the final sections, which occurred at substantially longer times and are not shown in Fig. 4, the plots merged into a common line with a gradient corresponding to a slightly slower

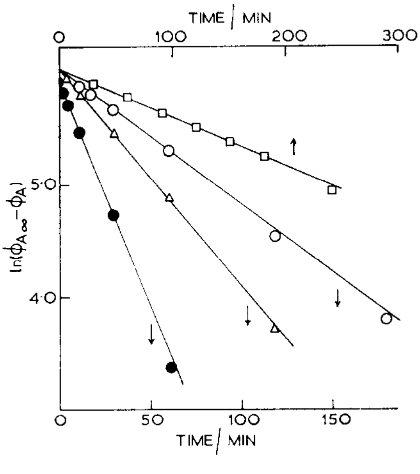

Fig. 3. Appropriate plots of ϕ_A to determine k with values of k_A/k_B of 1 (□), 5 (○), 10 (△), and 20 (●).

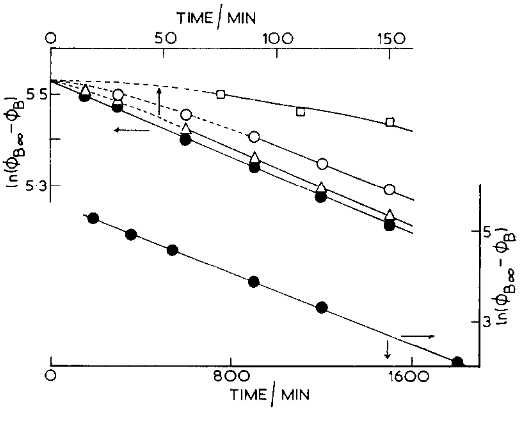

Fig. 4. Appropriate plots (upper and left-hand scales) of ϕ_B to determine k_B with values of k_A/k_B of 1 (□), 5 (○), 10 (△), and 20 (●); an extended plot for the last value is also shown for longer times (lower and right-hand scales).

rate of 0.56 D atoms/100 molecules min^{-1}.

It is clear that the HSK method gives a good estimate for the total rate of exchange and only fails in the extreme case where $k_A = k_B$ and the two groups of hydrogen atoms react at the same rate. In practice, the method would never be applied to such a case, which would be analyzed by standard methods (*7*).

The estimated values of k_B are all low compared with the chosen value, but the deviation is not greater than 10% if k_A/k_B is 5 or higher. The reason for the discrepancy is that the deuterium pool has become diluted as a result of the exchange of the first group by the time that the second group starts to react. The method makes no allowance for this, and consequently the calculated value for k_B will be slightly low. A correction for this factor could easily be made. The underestimation of k_B leads to a slight overestimation of the ratio k_A/k_B by about 10%, rising to 20% for $k_A/k_B = 5$.

It is fortunate that the HSK method is satisfactory for cases where it is possible to distinguish different groups of hydrogen atoms by inspection of the experimental results. Where such differences can be seen, corresponding to $k_A/k_B > 5$, reasonably accurate results for the rate constants can be obtained, the accuracy improving for higher values of k_A/k_B. The method only fails for cases where it is difficult to distinguish the different groups of atoms because they have similar reactivity.

This investigation has necessarily been limited to testing the HSK method for two groups of hydrogen atoms exchanging in a stepwise fashion because it is not feasible to calculate distributions of products involving multiple exchange. However, it seems probable that the HSK method will work at least as satisfactorily for cases of multiple exchange as it does for stepwise exchange. The determination of the total rate ($k = k_A + k_B$) should be as reliable for multiple exchange, and the estimation of k_B may even be improved because the multiple exchange would increase the production of d_4 at an early stage and enable the exchange of the second group to be followed more efficiently than with stepwise exchange.

The HSK method was put forward originally (*5*) for molecules containing three groups of hydrogen atoms. Our examination of its validity has been restricted to the case of two such groups because the theory for calculating distributions was available for only two groups. However, on the basis of the present work, it would be reasonable to assume that the HSK method can be applied to more groups provided the value of $k_L/k_M > 5$ for successive groups *L* and *M*. But corrections for isotopic dilution will be essential.

Temperature Programming

The method of generating "experimental data" was first tested for the case where all hydrogen atoms in the molecule exchange at equivalent rates. Values of ϕ at a series of values of t_l were obtained from data generated with a chosen activation energy of 40 kJ mol^{-1}, an initial rate of exchange of 1.0 D atoms/100 molecules min^{-1} at 273 K, and a rate of increase of temperature of 1.0 K min^{-1}. The average rate of reaction was evaluated for each time interval from

$$\bar{k} = \phi_\infty[\ln(\phi_\infty - \phi_{i+l}) - \ln(\phi_\infty - \phi_i)]/\Delta t_l \tag{2}$$

with ϕ_{i+l} and ϕ_i representing successive values of ϕ. Then ln $\bar{k}$ was plotted against the reciprocal of the mean temperature for each time interval. The fact that a good straight line was obtained with a gradient corresponding to an activation energy of 39.2 ± 0.8 kJ mol^{-1} confirmed that the method of generating data was satisfactory.

The method was next applied to the case of two groups of hydrogen atoms with values of $\bar{k}/\bar{k}_B$ of 6, 11, and 21, all activation energies being chosen as 40 kJ mol^{-1}. The "experimental data" were used to determine $\bar{k}$ and $\bar{k}_B$ by expressions analogous to Eq. (2) and the corresponding activation energies estimated from Arrhenius plots. The comparison between the estimated values of $\bar{k}/\bar{k}_B$ and the estimated activation energies with the respective chosen values was used to assess the validity of the method of handling the data from temperature-programmed catalysis. Some Arrhenius plots are shown in

TABLE 3

RESULTS FOR TEMPERATURE-PROGRAMMED CATALYSIS

$\bar{k}/\bar{k}_B$			E^a kJ mol^{-1}	
Chosen	Est. when $d_5 \simeq 10\%$	Est. when $d_5 \simeq 20\%$	for k	for k_B
21	22.6	22.2	41.4	40.3
11	13.5	13.1	42.6	37.3
6	7.7	7.4	43.8	33.4

[a] Chosen activation energies were 40 kJ mol^{-1} in all cases.

Fig. 5, and the results are summarized in Table 3.

Satisfactory straight lines were obtained from the Arrhenius plots for the total rate of exchange, and the agreement between the derived activation energies and the chosen value was better the higher the value of $\bar{k}/\bar{k}_B$.

The results for $\bar{k}_B$ were much less satisfactory, particularly for the lowest value of $\bar{k}/\bar{k}_B = 6$. The Arrhenius plot in this case was curved and only approximated a straight line at a comparatively late stage in the reaction. The derived activation energy from this line was too low, and the estimated values of $\bar{k}/\bar{k}_B$, whether determined when there was 10 or 20% of d_5 formed, were too high. Better results were obtained for $\bar{k}/\bar{k}_B = 11$ and the most satisfactory results for $\bar{k}/\bar{k}_B = 21$. The difficulties associated with the Arrhenius plots for $\bar{k}_B$ for the lower values of $\bar{k}/\bar{k}_B$ clearly arise from the type of behavior exhibited in Fig. 4 for the plots for $\bar{k}_B$ in the constant-temperature experiments. The estimates for $\bar{k}_B$ are much too low at the stage when the slower hydrogen atoms begin to exchange but become more reliable as the reaction proceeds.

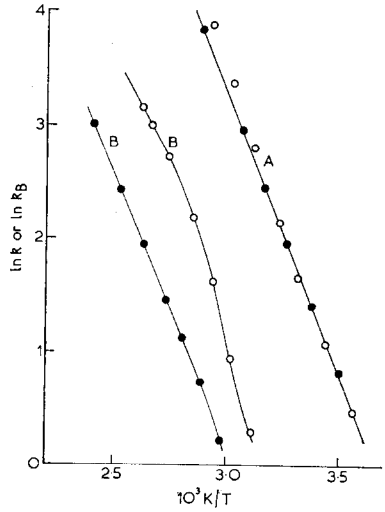

FIG. 5. Arrhenius plots for the estimated rates of exchange from temperature-programmed results with values of $\bar{k}/\bar{k}_B$ of 6 (○) and 21 (●); A represents $\bar{k}$, the total rate of exchange, and B the rate of the slower group, $\bar{k}_B$.

The conclusion is that the HSK method works satisfactorily for temperature-programmed catalysis when the ratio of the rate constants of the two groups of hydrogen is greater than about 20 and is definitely unreliable if the ratio is less than 10.

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