

Simple and Rapid Determination of the Activation Parameters of Organic Reactions by Temperature-Dependent NMR Spectroscopy II. Application to Reversible Reactions

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(Received April 22, 1996)

A non-isothermal (NIT) method for evaluating the activation enthalpies and entropies of reactions in solutions was applied to several reversible reactions. This was realized by a stepwise elevation of the temperature of a reaction system using a variable-temperature apparatus comprising an NMR spectrometer and a quick collection of FID (free induction decay) at every plateau of the step. The rate from NIT experiments agreed well with the previously measured rates by the conventional methods.

A conventional method to measure the activation energies and entropies of reactions is based on the Arrhenius plot, $\log k$ vs. $(1/T)$ plot, which is drawn by repeating of the measurements of the rates (k) as a function of the temperature (T). This method has been widely applied to various reactions having moderate rates. However, it needs several repetitions of the measurements at various temperatures in order to draw an Arrhenius plot. Thus, the determining the activation parameters sometimes becomes difficult when either the sample is very precious or the reaction proceeds very slowly. Previously, theoretical treatments of the kinetic analysis of a non-isothermal (NIT) process under a programmed variation of the temperature have been reported by several investigators.¹⁻⁶ However, the application of the method is limited to a solid-state process and to few very simple reactions, because of formulation and calculation complexities.

We recently re-examined the NIT kinetic method, and improved the method so as to be applicable to general organic reactions.^{7,9} Our method for the analyzing the NIT reaction process consists of a stepwise elevation and depression of the temperature in the course of a NMR measurement (NIT-NMR method). In order to examine the reliability of this method, it was first applied to some irreversible organic reactions, whose activation quantities from the conventional Arrhenius plots has been known. In this study, the NIT-NMR method was applied further to some reversible reactions.

Theory and General Method

A rather general treatment of the NIT kinetic data has been reported by Katoh and co-workers.³ They applied it to reactions under a uniform rate of elevation of the temperature, i.e. a linearly programmed elevation of the temperature.

In NIT experiments, the concentration (C) of the product, or the reactant, after a reaction period (t), cannot be determined from the temperature (T) alone, but is dependent on

how the temperature changes as a function of time. In the case of reversible first-first-order reactions,



C (in Eq. 2) cannot be evaluated without knowing the temperature as a function of time. Thus, the rate equation for Eq. 1 can be written as follows:^{7,8)}

$$(dC_B/dt) = k_1(t)C_A - k_{-1}(t)C_B \quad (2)$$

Similarly, the rate of a second-second-order reversible reaction,



can be expressed by Eq. 4,^{7,8)}

$$(dC_C/dt) = k_1(t)C_A C_B - k_{-1}(t)C_C C_D \quad (4)$$

Equations 2 and 4 could be re-written using the equilibrium constant ($K(t)$) at time t , as given by Eq. 2a for first-first-order reversible reactions, and by Eq. 4a for second-second-order reversible reactions:

$$k_1(t) = (dC_B/dt)/[C_A - C_B/K(t)], \quad k_{-1}(t) = k_1(t)/K(t) \quad (2a)$$

and

$$k_1(t) = (dC_C/dt)/[C_A C_B - C_C C_D/K(t)], \\ k_{-1}(t) = k_1(t)/K(t), \quad (4a)$$

where $K(t) = k_1(t)/k_{-1}(t)$.

The equilibrium constants in Eqs. 2a and 4a could be determined by independent experiments. Exactly in the same way as the experiments concerning irreversible reactions, the variable-temperature NMR apparatus was operated so as to

raise the temperature of the sample probe stepwise at regular intervals (τ) (Fig. 1).⁹⁾

Calculations of the activation parameters were achieved with a very good approximation by replacing the stepwise $T-t$ curve by a $T-t$ line passing through the center of every plateau (N_1, N_2, \dots, N_i). Actually, the NMR spectra of the reaction system were measured at the end of every plateau (M_1, M_2, \dots, M_i) of the temperature (where $T=T_1, T_2, \dots, T_i$). The corrected temperature (T_{s_i}) can be described by Eq. 5, where the plus sign is for a stepwise elevation, the minus sign is for a stepwise depression of T and κ is a correction term of the temperature, which corresponds to the deviation in the temperature (MP_1, MP_2, \dots, MP_i):

$$\kappa = \pm \Delta T / 2 [\tau_1 / (\tau_1 + \tau_N)]. \quad (5)$$

The $C-t$ curve was then simulated by

$$C(t) = a_0 + \sum a_m t^m \quad (6)$$

and

$$dC(t)/dt = \sum m a_m t^{m-1}, \quad (7)$$

where a_m are parameters calculated by a multiple-regression analysis.

Actually, the summation up to $m=4$ gives sufficiently accurate results. The best-fit parameters ($a_0 \dots a_m$) could be calculated by a linear least-squares calculation. Thus, the rate constant at any temperature can be obtained from Eq. 7, derived as the first derivative of Eq. 6. These calculations can be easily carried out numerically.

The NIT experiments were generally carried out as reported in our previous paper.⁹⁾ Usually, NMR data were collected at more than six different temperatures in a run in order that reliable least-squares determination of ($a_0 \dots a_m$) in Eqs. 6 and 7 could be achieved. The rate data necessary for the estimating the activation parameters were calculated at every point of the NMR data collection, except for the end points. Since the gradient at the highest-conversion-end point is not interpolated by the two data points, it was ignored in order to obtain a reliable gradient (dC/dt). From the thus obtained rate data, activation quantities were calculated using the usual Arrhenius equation.

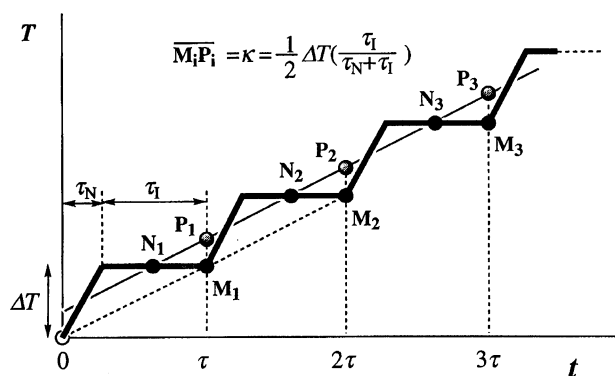


Fig. 1. Diagram of the stepwise non-isothermal (elevation temperature) curve and the derivation of a correction term.

Experimental

General Procedures. All of the compounds used in the kinetic measurements were known and purchased commercially. The deuterium-labelled solvents were also commercially available.

Variable-temperature ^1H NMR spectra were obtained on a JEOL-EX270 NMR spectrometer equipped with a JEOL EVTS-3 variable-temperature apparatus.

Determination of τ_N of the Variable-Temperature Apparatus.

The τ_N value is inherent to the employed variable-temperature apparatus, and was determined by measuring the temperature of the reaction system as a function of time under the conditions of the operation of temperature elevation. Routine measurements were carried out under the following conditions: $\Delta T = +5.0$ K, $\tau_1 = 5.10$ min, and $\tau_N = 1.40$ min.

Measurements. The procedure was illustrated by the example of the iodination of ethyl bromide by lithium iodide. This reaction was previously shown to proceed reversibly under the usual time-scale of measurement. A 5 mm ϕ sample tube containing 2.5×10^{-2} mmol of ethyl bromide (2.7 mg) and 0.60 ml (0.523 g) of acetone- d_6 (as a solvent) was kept in the NMR sample probe maintained at 25 °C for more than 5 min. Then, an amount (1.3×10^{-2} mmol, 1.7 mg) of lithium iodide (the less volatile reactant), which was dissolved in the same solvent and kept in a thermostatic bath at 25 °C, was quickly added into the sample tube. This could be completed within 5 s, and the time was started at this moment ($t=0$).

After the shim of the magnet was adjusted within two minutes, the FID was accumulated 4 times under the following conditions: acquisition time, 3.031 s; pulse delay, 3.969 s; repetition time, 7.0 s; pulse width, 6 μs ; and data points, 32876. The collected data were stored on a hard disk for the calculating the rates and the activation parameters. All of these operations were completed within τ_1 (this actually needed 3.25 min, in this case, while $\tau_1 = 5.10$ min). The temperature of the system was raised to 30 °C (when $\Delta T = 5.0$ K). After an elapsed time longer than τ_1 , exactly the same operations were repeated. After seven repetitions, the temperature reached 55 °C, when the measurement was completed after the final collection of FIDs.

Using previously set parameters ($\tau_N = 1.40$ min, $\tau_1 = 5.10$ min, and $\Delta T = 5.0$ K), Eq. 5 gave a κ value of 1.96 K; thus $T_s = T_{\text{obs}} + 1.96$.⁹⁾ The time-conversion data given in Table 1 were fitted to the polynomial equation (Eq. 5) by a least-squares calculation using multiple-regression analysis program.¹⁴⁾ Thus, the best-fit equation obtained and its first derivative are given by Eqs. 6a and 7a, respectively, where t is measured in minutes:

$$C_{\text{pr}} = (0.0) + (5.00 \times 10^{-5})t + (9.74 \times 10^{-6})t^2 - (1.44 \times 10^{-7})t^3 \quad (6a)$$

and

$$dC_{\text{pr}}/dt = (5.00 \times 10^{-5}) + (1.95 \times 10^{-5})t - (4.32 \times 10^{-3})t^2. \quad (7a)$$

The rate (dC_{pr}/dt) should be calculated using the following equation at any temperature: where $k_1(t)$ is a rate constant for forward reaction and $k_{-1}(t)$ is a rate constant for backward reaction.

$$dC_{\text{pr}}/dt = k_1(t)C_{\text{EtBr}}C_{\text{LiI}} - k_{-1}(t)C_{\text{pr}}^2, \quad (8)$$

where $k_1(t)$ is a rate constant for forward reaction and $k_{-1}(t)$ is a rate constant for backward reaction.

By using the time- T_s relationship and Eq. 8a

$$k_1(t) = (dC_{\text{pr}}/dt) / [C_{\text{EtBr}}C_{\text{LiI}} - C_{\text{pr}}^2/K(t)]$$

$$k_{-1}(t) = k_1(t)/K(t), \quad (8a)$$

Table 1. Time-Conversion Data for the Reaction of Ethylbromide with Lithium Iodide

Time	Conversion	$C_{pr}^{a)}$	$T_s - 273.15$	k_1	k_{-1}
		mmol dm ⁻³	°C	dm ³ mol ⁻¹ min ⁻¹	
5'50''	0.0	0.0	26.76	5.83×10^{-2}	4.83×10^{-1}
12'20''	1.67×10^{-3}	1.95	31.76	3.15×10^{-1}	2.45
18'50''	7.94×10^{-3}	3.29	36.76	4.49×10^{-1}	3.32
25'20''	1.25×10^{-2}	5.20	41.76	7.09×10^{-1}	4.96
31'50''	1.66×10^{-2}	6.89	46.76	1.41	9.35
38'20''	1.96×10^{-2}	8.12	51.76	22.2	140
44'50''	2.13×10^{-2}	8.84	56.76	-2.37	-0.70

a) The concentration of product can be calculated by $C_{pr} = (C_{react}^0)/(1 + I_{react}/I_{pr})$, where C_{react}^0 , I_{react} and I_{pr} are the initial concentration of a reactant, the intensity of NMR signal of the reactant and the intensity of NMR signal of the product.

the rate constant at every T_s could be evaluated. In Eqs. 8 and 8a, C_{pr} , C_{EtBr} , and C_{LiI} refer, respectively, to the concentrations of the product (lithium bromide or ethyl iodide), ethyl bromide, and lithium iodide, where $K(t)$ is the equilibrium constant which is equal to $k_1(t)/k_{-1}(t)$.

Thus, obtained sets of k and T_s give the activation quantities upon applying the Arrhenius equation. However, what must be noticed is that the end point was ignored in order to obtain a reliable gradient (dC/dt). Also the equilibrated point must be excluded, which can be evaluated from the linearity of $\ln k_i$ vs. T_s^{-1} (Fig. 2).

Three points in Table 3 [two end points ($t=0.0$ min, 44 min 50 s) and the equilibrated point (38 min 20 s)] are excluded in the calculation of the Arrhenius parameters from the NIT-NMR analysis. The equilibrated points are ineffective for the determining of the activation parameters and apparently reduce their precision. Thus, the measurements should be carried out in the region of the concentration far from equilibrium, practically at the lower temperature region. The enthalpies and entropies of activation were calculated from the Arrhenius parameters for the forward and backward reactions.

The magnitude of temperature elevation (or depression) (ΔT) is usually constant throughout an experiment, even though the data can be analyzed with much labor in the case of a regularly varied temperature gap.

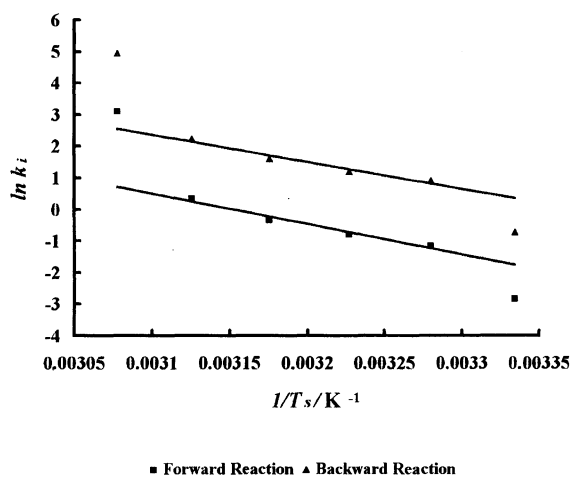


Fig. 2. The $\ln k$ vs. T_s^{-1} plot for the reaction of Eq. 1.

Results and Discussion

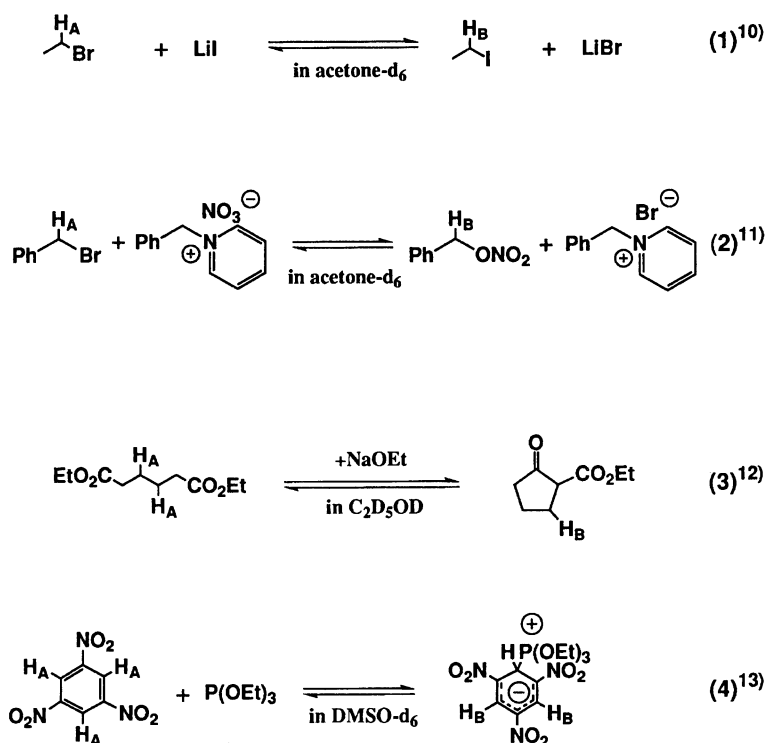
In order to examine the validity of our NIT method, we determined the activation parameters for several organic reversible reactions (Scheme 1), whose activation parameters were previously determined by a well established conventional method. These test reactions were carefully selected on the basis of the criteria given in our previous paper.⁸⁾ The amount of reactant (A) and product (B) were determined from the integrated intensities of the key band signals, H_A and H_B , respectively. These hydrogen atoms are specified in Scheme 1, and their chemical shifts are given in Table 2. In the case of applying the NIT method to a reversible reaction, we need the equilibrium constant in addition to the NIT data. This is a noticeable difference from the application to irreversible reactions. In order to ascertain the validity of the reported equilibrium constants, the equilibrium constants were determined independently by the NMR method. The results are given in Table 3. Our equilibrium constants agreed with the reported values^{10,11)} for reactions 1 and 2 (Table 4). However, the difference between the two data are beyond the experimental errors for reactions 3 and 4. Thus, the equilibrium constants from our NMR measurements were used in all series of NIT-NMR analysis. They were measured under exactly the same conditions as the NIT measurements, and, hence, should be more suitable.

The NIT activation quantities, ΔH^\ddagger and ΔS^\ddagger , were calculated from the $C-t$ curve and its first derivative obtained by the procedures in the experimental section, and given in Table 5 together with the corresponding reported values¹⁰⁻¹³⁾ from the Arrhenius method.

The NIT activation quantities for reactions 1 and 2 agreed

Table 2. The Key Band NMR Signals for the Determination of the Reactants and the Products in the Reversible Reaction

Eq. No.	δ (H_A)	δ (H_B)
1	3.49 (2H, q, $J=7.3$ Hz)	3.26 (2H, q, $J=7.5$ Hz)
2	4.65 (2H, s)	5.59 (2H, s)
3	2.33 (4H, t, $J=9.9$ Hz)	2.14 (2H, t, $J=6.9$ Hz)
4	9.17 (3H, s)	8.26 (2H, s)



Scheme 1. Selected reversible organic reactions.

Table 3. Equilibrium Constants ($K \times 10$) Determined by NMR Method for the Reaction in Scheme 1

Eq. No.	K						ΔK^a
	24.8 °C	29.8 °C	34.8 °C	39.8 °C	44.8 °C	49.8 °C	
1 ^{b)}	1.26	1.35	1.44	1.54	1.64	1.75	
Ref. ¹⁰⁾	1.17	1.25	1.32	1.40	1.48	1.56	+0.09
2 ^{b)}	1.321	1.325	1.328	1.331	1.334	1.337	
Ref. ¹¹⁾	1.244	1.247	1.251	1.254	1.257	1.260	+0.06
3 ^{b)}	3.71	3.80	3.89	3.98	4.06	4.15	
Ref. ¹²⁾	2.80	3.14	3.50	3.90	4.33	4.79	-0.89
4 ^{c)}	2.10×10^3	2.55×10^3	3.07×10^3	3.68×10^3	4.39×10^3	5.21×10^3	
Ref. ¹³⁾	6.21×10^3	7.26×10^3	8.45×10^3	9.78×10^3	1.13×10^4	1.29×10^4	-0.63

a) Average relative errors (ΔK) are the average over the number of data of relative errors (ΔK) calculated by $(K_{\text{NMR}} - K_{\text{IT}})/K_{\text{IT}}$, where K_{NMR} is equilibrium constant obtained by NMR method and K_{IT} is equilibrium constant from the literature. b) Unit is [dimensionless]. c) Unit is [$\text{dm}^3 \text{mol}^{-1}$].

Table 4. The Thermodynamic Quantities Determined by NMR in Comparison with Those in Literatures

Eq. No.	NMR (Present work)		Isothermal (Literature) ⁹⁻¹²⁾		Difference	
	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J mol}^{-1} \text{K}^{-1}$	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J mol}^{-1} \text{K}^{-1}$	$\Delta \Delta H$	$\Delta \Delta S$
1	11 ± 0.2	18 ± 0.7	$9.1 \pm 0.3^{10)}$	$13 \pm 0.9^{10)}$	+1.9	+5
2	-0.38 ± 0.3	-16 ± 0.9	$-0.43^{11)}$	$-16^{11)}$	+0.05	0
3	3.5 ± 0.2	3.5 ± 0.5	$17 \pm 0.7^{12)}$	$66 \pm 2.2^{12)}$	-13.5	-62.5
4	29 ± 0.9	123 ± 2.8	$23^{13)}$	$113^{13)}$	+6.0	+10

with the reported values, while the NIT values showed a considerably large disagreement from those in the literature for reactions 3 and 4. Thus, we re-determined the activation quantities by the conventional Arrhenius method. The results are also given in Table 5. Our new data agree far better than the old reported values.^{12,13)} Thus, the new activation quantities were used for the purpose of comparing with the

NIT quantities of reactions 3 and 4.

The experimental errors for the NIT activation parameters, [$\text{SD}(\Delta H^\ddagger) = 2.7$ and $\text{SD}(\Delta S^\ddagger) = 3.5$], were nearly equal to these for the Arrhenius method [$\text{SD}(\Delta H^\ddagger) = 2.0$ and $\text{SD}(\Delta S^\ddagger) = 6.0$]. Added to this, the standard deviations for the difference ($\Delta \Delta H^\ddagger$ and $\Delta \Delta S^\ddagger$) in the NIT and Arrhenius values are 0.80 kJ mol^{-1} and $4.0 \text{ J mol}^{-1} \text{K}^{-1}$. The deviations be-

tween the Arrhenius and NIT activation quantities are within the experimental errors of both the Arrhenius and NIT data. Thus, the NIT experiments have been shown to provide activation parameters as accurate as those from Arrhenius plots.

A statistical treatment for the difference in the NIT and Arrhenius activation parameters gives the following good confidence intervals of the standard deviation at the 99% confidence level, namely $SD(\Delta\Delta H^\ddagger, 99\%) = 0.50\text{--}2.3 \text{ kJ mol}^{-1}$

Table 5. Comparison of the NIT and the Arrhenius Activation Quantities for Various Reactions for Reversible Reactions

Eq. No. ^{a)}	NIT (Present work)		Arrhenius		Difference	
	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{ K}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{ K}^{-1}$	$\Delta\Delta H^\ddagger$	$\Delta\Delta S^\ddagger$
1F	77.8±7.6	-34.4±24	77.4±0.1 ¹⁰⁾	-38.6±0.3 ¹⁰⁾	+0.4	+4.2
1B	68.3±7.6	-47.1±24	68.3±0.3 ¹⁰⁾	-51.3±0.9 ¹⁰⁾	+0.4	+4.2
2F	72.8±6.0	-72.1±19	72.9 ¹¹⁾	-73.8 ¹¹⁾	-0.1	+1.7
2B	73.2±6.0	-56.3±19	74.4 ¹¹⁾	-57.4 ¹¹⁾	-1.2	+1.1
3F	74.2±4.4	-78.7±14	[74.3±0.1 105±17 ¹²⁾	-78.7±0.4 -0.30±53 ¹²⁾	-0.1 -31	+0.0] ^{b)} -78
3B	70.7±4.4	-82.2±14	[70.8±0.1 88.7±16 ¹²⁾	-82.0±0.3 -63.6±49 ¹²⁾	-0.2 -18	-0.2] ^{b)} -19
4F	43.0±0.3	-172±0.8	[41.8±4.6 70.3±2.1 ¹³⁾	-176±15 -62.8±8.4 ¹³⁾	+1.1 -27	+4.2] ^{b)} -109
4B	12.6±0.3	-299±19	[13.0±4.1 46.8±2.1 ¹³⁾	-298±12 -176±38 ¹³⁾	-0.4 -34	-1.1] ^{b)} -123

a) F and B indicates the forward and the backward reactions, respectively. b) The activation parameters determined by the Arrhenius-NMR method in this work are given in brackets.

Table 6. Comparison of Rate Constants ($k \times 10^3$) by the NIT and the Arrhenius Methods for the Reactions in Scheme 1

Eq. No.	k^c						$\Delta\bar{k}^a$	
	Temp	24.8 °C	29.8 °C	34.8 °C	39.8 °C	44.8 °C		49.8 °C
1F		1.4×10^2	2.4×10^2	4.0×10^2	6.5×10^2	1.1×10^3	1.7×10^3	+0.43
Ref. ¹⁰⁾		9.7×10^1	1.7×10^2	2.8×10^2	4.6×10^2	7.4×10^2	1.2×10^3	
1B		1.2×10^3	1.9×10^3	3.1×10^3	4.7×10^3	7.2×10^3	1.1×10^4	+0.43
Ref. ¹⁰⁾		3.4×10^2	3.8×10^2	4.3×10^2	4.8×10^2	5.3×10^2	5.9×10^2	
2F		1.1×10^1	1.8×10^1	2.9×10^1	4.7×10^1	7.4×10^1	1.2×10^2	+0.29
Ref. ¹¹⁾		8.5	1.4×10^1	2.3×10^1	3.7×10^1	5.8×10^1	9.0×10^1	
2B		6.1×10^1	1.0×10^2	1.6×10^2	2.6×10^2	4.2×10^2	6.5×10^2	+0.80
Ref. ¹¹⁾		3.4×10^1	5.5×10^2	9.1×10^2	1.5×10^1	2.3×10^1	3.7×10^1	
3F		2.8	4.7	7.7	1.2×10^1	2.0×10^1	3.1×10^1	+11.8
Ref. ¹²⁾		1.4×10^{-1}	2.9×10^{-1}	5.8×10^{-1}	1.1	2.2	4.1	
3B		7.6	1.2×10^1	1.9×10^1	3.1×10^1	4.9×10^1	7.5×10^1	+118
Ref. ¹²⁾		4.9×10^{-2}	9.0×10^{-2}	1.6×10^{-1}	2.9×10^{-1}	5.0×10^{-1}	8.5×10^{-1}	
3F'		2.7	4.5	7.3	1.2×10^1	1.9×10^1	3.0×10^1	(+0.05) ^{b)}
3B'		7.6×10^1	1.2×10^1	2.0×10^1	2.6×10^1	3.5×10^1	4.5×10^1	(+0.05) ^{b)}
4F		1.1×10^1	1.5×10^1	2.0×10^1	2.6×10^1	3.5×10^1	4.5×10^1	-0.92
Ref. ¹³⁾		9.3×10^1	1.5×10^2	2.4×10^2	3.8×10^2	5.9×10^2	9.1×10^2	
4B		5.1×10^{-1}	5.7×10^{-1}	6.2×10^{-1}	6.9×10^{-1}	7.5×10^{-1}	8.2×10^{-1}	-0.79
Ref. ¹³⁾		1.5	2.1	2.8	3.9	5.3	7.0	
4F'		1.1×10^{-1}	1.5×10^{-1}	6.2×10^{-1}	6.9×10^{-1}	7.5×10^{-1}	8.2×10^{-1}	(+0.07) ^{b)}
4B'		5.1×10^{-1}	5.7×10^{-1}	6.3×10^{-1}	6.9×10^{-1}	7.5×10^{-1}	8.2×10^{-1}	(+0.02) ^{b)}

a) Average relative error ($\Delta\bar{k}$) is the average over the number of data of relative errors (Δk) calculated by $(k_{\text{NIT}} - k_{\text{IT}})/k_{\text{IT}}$, where k_{NIT} is rate constant by NIT-NMR method and k_{IT} is rate constant by the Arrhenius method. b) Average relative errors obtained by our isothermal NMR method are given in parentheses. c) Unit of k -values in Eq. No. 1F, 1B, 2F, 2B, 4F and 3F, 3B, 4B are [$\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$] and [min^{-1}], respectively.

and $SD(\Delta\Delta S^\ddagger, 99\%)=1.3\text{--}5.7\text{ kJ mol}^{-1}\text{ K}$. A significance test (the test for equality between two means or variances), assuming a significance level of 1% showed that there is no significant difference between the activation parameters from the two methods.

The rate-constant values (k) and their average relative errors ($\Delta\bar{k}$) obtained from the activation parameters of the NIT and the Arrhenius method are given in Table 6. The confidence intervals of the standard-deviation values at 99% confidence level are $SD(\Delta\bar{k})=0.20\text{--}0.35$. The significance test (the test for equality between two means or variances), assuming a significance level of 1%, showed that there is no significant difference between the k -values from the two methods. The statistical significance tests mentioned above also guarantee the validity for a reversible reaction of our NIT experiments.

In conclusion, the NIT-NMR method for the determining the activation quantities are shown to be applicable to reversible reactions. Only a time-programmed variable-temperature measurement gives the activation quantities to nearly the same accuracy as does the conventional Arrhenius method. In practicing this determination, however, the order of the reaction and equilibrium constant need to be preliminarily determined.

The authors are grateful to Professors Masahiro Nakada and Iwao Amasaki, Chiba Institute of Technology, for their advices throughout this work. They also thank Professor Kazuhisa Sakakibara for his encouragement.

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8) By the integration of Eq. 2 at $C_A^0 \neq 0$ and $C_B^0 = 0$, Eq. 9 was derived.

$$C_B(t) = C_A^0 \left[\int_0^t (K(s)/(K(s)+1)k(s) \exp\left(-\int_s^t k(t)dt\right) ds \right], \quad (9)$$

where C_A^0 is the initial concentration of A, $k(t)=k_1(t)+k_{-1}(t)$ and $K(s)$ is equilibrium constants at time s .

Similarly the integration of Eq. 4 at $C_A^0 \neq 0$, $C_B^0 \neq 0$, $C_C^0 = 0$, and $C_D^0 = 0$ gave the concentration of the product as a function of time (t).

$$C_C = \int_0^t \left[\alpha(s)\beta(s)\gamma(s)\{\alpha(s) - \beta(s)\} \exp\left(-\int_s^t \gamma(t)dt\right) / \left\{ \beta(s) \exp\left(-\int_s^t \gamma(s)dt\right) - \alpha(s)^2 \right\} \right] ds, \quad (10)$$

where $\alpha(s)$, $\beta(s)$, and $\gamma(s)$ is

$$\alpha(s) = K(s) \frac{[(C_A^0 + C_B^0) - \sqrt{(C_A^0 + C_B^0)^2 - 4(1 - 1/K(s))C_A^0 C_B^0}]/[2(K(s) - 1)]}{},$$

$$\beta(s) = K(s) \frac{[(C_A^0 + C_B^0) + \sqrt{(C_A^0 + C_B^0)^2 - 4(1 - 1/K(s))C_A^0 C_B^0}]/[2(K(s) - 1)]}{},$$

$$\gamma(s) = \{\alpha(s) - \beta(s)\}\{k_1(t) - k_{-1}(t)\}.$$

Further, $K(s)$ is the equilibrium constant at time s and C_A^0 and C_B^0 are the initial concentrations for the reactants A and B, respectively.

However, Eqs. 9 and 10 did not allow us to derive any formula of C useful to the analysis of the rate and activation quantities. For this reason, the C - t curve was treated numerically with rate equation.

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